Toxic Metal Recovery from Spent Hydroprocessing Catalyst

By

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ABSTRACT

Spent hydroprocessing catalysts (HPCs) are solid wastes generated in refinery industries and typically contain various hazardous metals, such as Co, Ni, and Mo. These wastes cannot be discharged into the environment due to strict regulations and require proper treatment to remove the hazardous substances. Various options have been proposed and developed for spent catalysts treatment; however, hydrometallurgical processes are considered efficient, cost-effective and environmentally-friendly methods of metal extraction, and have been widely employed for different metal uptake from aqueous leachates of secondary materials. Although there are a large number of studies on hazardous metal extraction from aqueous solutions of various spent catalysts, little information is available on Co, Ni, and Mo removal from spent NiMo hydroprocessing catalysts.

In the current study, a solvent extraction process was applied to the spent HPC to specifically remove Co, Ni, and Mo. The spent HPC is dissolved in an acid solution and then the metals are extracted using three different extractants, two of which were amine-based and one which was a quaternary ammonium salt. The main aim of this study was to develop a hydrometallurgical method to remove, and ultimately be able to recover, Co, Ni, and Mo from the spent HPCs produced at the petrochemical plant in Come By Chance, Newfoundland and Labrador. The specific objectives of the study were: (1) characterization of the spent catalyst and the acidic leachate, (2) identifying the most efficient leaching agent to dissolve the metals from the spent catalyst; (3) development of a solvent extraction procedure using the amine-based extractants Alamine308, Alamine336 and the quaternary ammonium salt, Aliquat336 in toluene to remove Co, Ni, and Mo from the spent catalyst;

(4) selection of the best reagent for Co, Ni, and Mo extraction based on the required contact time, required extractant concentration, as well as organic:aqueous ratio; and (5) evaluation of the extraction conditions and optimization of the metal extraction process using the Design Expert® software.

For the present study, a Central Composite Design (CCD) method was applied as the main method to design the experiments, evaluate the effect of each parameter, provide a statistical model, and optimize the extraction process. Three parameters were considered as the most significant factors affecting the process efficiency: (i) extractant concentration, (ii) the organic:aqueous ratio, and (iii) contact time. Metal extraction efficiencies were calculated based on ICP analysis of the pre- and post–leachates, and the process optimization was conducted with the aid of the Design Expert® software.

The obtained results showed that Alamine308 can be considered to be the most effective and suitable extractant for spent HPC examined in the study. Alamine308 is capable of removing all three metals to the maximum amounts. Aliquat336 was found to be not as effective, especially for Ni extraction; however, it is able to separate all of these metals within the first 10 min, unlike Alamine336, which required more than 35 min to do so.

Based on the results of this study, a cost-effective and environmentally-friendly solvent-extraction process was achieved to remove Co, Ni, and Mo from the spent HPCs in a short amount of time and with the low extractant concentration required. This method can be tested and implemented for other hazardous metals from other secondary materials as well. Further investigation may be required; however, the results of this study can be a guide for future research on similar metal extraction processes.

Dedication

I dedicate my M.Sc. dissertation to my parents, Maliheh and Mohammad Reza, whose ongoing love and support have continuously motivated me to achieve higher levels of education.

I also dedicate this thesis to my lovely husband, Hesam, who has always believed in me. None of this would have happened without his help and constant encouragement.

I would also like to dedicate this dissertation to my kind and knowledgeable supervisor and mentor, Dr. Paris Georghiou who supported me and has been amazingly helpful since the beginning of my program.

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Table of Contents:

Abstract		ii
Dedication		iv
Acknowledgment		v
Table of Contents		vi
List of Tables		xi
List of Figures		xiii
List of Symbols and Abbreviation		xvii
Chapter 1 Introduction		1
1.1	Background and motivation	1
1.2	Problem statement	3
1.3	Objectives of the research	4
1.4	Approach	5
1.5	Outline of the thesis	6
Chapter 2 Literature Review		7
2.1	Overview	7
2.2	HPCs	7
2.2.1	Usage in petrochemical industries	7

2.2.2 Composition of HPCs 9

2.3 Deactivation and regeneration of HPCs 10

2.3.1 Extending the lifecycle of HPCs 14

2.3.2 Regeneration of HPCs 15

2.4 Environmental aspects of spent HPCs 17

2.4.1 Disposal regulations 18

2.4.2 Catalyst contamination 19

2.4.3 Handling of spent HPCs 21

2.4.4 Pollution prevention techniques 22

2.4.5 From preparation to disposal (cradle-to-grave approach) 23

2.5 Treatment of spent HPCs (metal removal and recovery) 27

2.5.1 Chlorination 28

2.5.2 Leaching 29

2.5.3 Biosorption 31

2.5.4 Hydrometallurgical processes 31

2.6 Response Surface Methodology (RSM) 34

Chapter 3 Materials and Methods 36

3.1 Overview 36

3.2 Apparatus and facilities 36

3.3 Materials 37

3.4 General experimental procedure 41

3.5 Design of experiments 42

3.6 Prediction of hazardous metal removal using Design Expert® 45

3.7 Analysis of variance (ANOVA) 46

3.8 Optimization 46

Chapter 4 Results and discussion 48

4.1 Overview 48

4.2 Spent catalyst characterization 48

4.3 Leaching results 51

4.4 Solvent extraction results 53

4.5 Effect of Aliquat336 on Co, Ni and Mo removal 55

4.5.1 Effect of Aliquat336 concentrations 56

4.5.2 Effect of organic:aqueous (O/A) ratios 58

4.5.3 Effect of contact times 60

4.5.4 Prediction of Co, Ni and Mo removal using Aliquat336 62

4.5.5 Optimization 63

4.6	Effect of Alamine308 on Co, Ni and Mo removal	63
4.6.1	Effect of Alamine308 concentrations	64
4.6.2	Effect of organic:aqueous (O/A) ratios	67
4.6.3	Effect of contact times	69
4.6.4	Prediction of Co, Ni and Mo removal using Alamine308	71
4.6.5	Optimization	71
4.7	Effect of Alamine336 on Co, Ni and Mo removal	72
4.7.1	Effect of Alamine336 concentrations	72
4.7.2	Effect of organic:aqueous (O/A) ratios	75
4.7.3	Effect of contact times	77
4.7.4	Prediction of Co, Ni and Mo removal using Alamine336	79
4.7.5	Optimization	79
4.8	Final remarks and other applications	80
Chapter 5 Conclusion		81
5.1	Concluding remarks	81
5.2	Significant scientific findings	82
5.3	New perspectives and recommendations	83

References 86

Appendix A: ANOVA results 92

Appendix B: List of publications and presentations 96

List of Tables

Table 2.1 - Relative effects of coke and metals deposition on the deactivation of HPCs in three typical reactions. 11

Table 3.1 -Information on solid spent HPC composition obtained from MSDS data as provided by North Atlantic Limited. 38

Table 3.2 - Composition of Aliquat336, Alamine308, and Alamine336, employed as extractant. 39

Table 3.3 - Process variables and their limit values. 43

Table 3.4 - Designed experiments using face-centered central composite design. 44

Table 4.1 - Leached amounts (in mg/L) of spent HPCs metals in three different acidic solutions. 52

Table 4.2 - Experimental results obtained by ICP-EOS based upon the designed experiments shown in Table 3.4 for Co, Ni and Mo extraction. 54

Table A.1 - Analysis of variance results for Ni extraction by Aliquat336. 93

Table A.2 - Analysis of variance results for Mo extraction by Aliquat336. 93

Table A.3 - Analysis of variance results for Ni extraction by Alamine308. 93

Table A.4 - Analysis of variance results for Mo extraction by Alamine308. 94

Table A.5 - Analysis of variance results for Co extraction by Alamine336. 94

Table A.6 - Analysis of variance results for Ni extraction by Alamine336. 94

Table A.7- Analysis of variance results for Mo extraction by Alamine336. 95

List of Figures

Figure 2.1 - Typical S-shaped catalyst deactivation curve (*top*), and typical activity loss curve for an HPC vs. time on stream (*bottom*). 13

Figure 2.2 – Deposited coke on HPCs as a function of the content of resins and asphaltenes according to three experimental samples for $NiMo/Al_2O_3$ catalysts at 8.5 MPa of H_2 and 673 K. 14

Figure 2.3 – The withdrawal system of spent HPCs from fixed bed reactors. 22

Figure 2.4 - Sulfided Co/Mo catalyst on alumina support showing the Co tetrahedrally coordinated at the edge of a single layer of MoS_2. 24

Figure 2.5 – Hydroprocessing production to disposal. 25

Figure 2.6 – The cradle-to-grave approach for HPCs. 26

Figure 2.7 - Metal extraction using acid. 30

Figure 2.8 - Single-stage batch solvent extraction process where an acid (aqueous) solution becomes in contact with an organic phase rich of the extractant. 33

Figure 3.1 – Spent HPC in powder form before any treatment, as provided by North Atlantic Refining Limited. 37

Figure 3.2 – General molecular structures of (a) tri-N-C8-10-alkyl amines (Alamine336), and (b) triisooctylamine (Alamine308). 40

Figure 3.3 - Chemical structure of Aliquat336 as its quaternary ammonium chloride salt 40

Figure 4.1 – SEM image of powdered spent catalyst showing coke on active surface of the spent HPC sample used in this study. 49

Figure 4.2 – Energy Dispersive X-ray spectroscopy (EDX) on the spent HPC surface showing the metals identified. 50

Figure 4.3 – *Left*: Freshly-prepared aqua regia. *Right*: Leachate after dissolution of spent HPC sample. 52

Figure 4.4 – Changes of extraction efficiencies for Co with the changes in Aliquat336 concentrations (O/A ratio 1.75 and contact time 65 min). 57

Figure 4.5 – Changes of extraction efficiencies for Ni with the changes in Aliquat336 concentrations (O/A ratio 1.75 and contact time 65 min). 57

Figure 4.6 – Changes of extraction efficiencies for Mo with the changes in Aliquat336 concentrations (O/A ratio 1.75 and contact time 65 min). 58

Figure 4.7 – Effect of O/A ratios on Co extractions (Aliquat336 concentration 0.305M and contact time 65 min). 59

Figure 4.8 – Effect of O/A ratios on Ni extractions (Aliquat336 concentration 0.305M and contact time 65 min). 59

Figure 4.9 – Effect of O/A ratios on Mo extractions (Aliquat336 concentration 0.305M and contact time 65 min). 60

Figure 4.10 – Co extractions vs. contact times (Aliquat336 concentration 0.305 M and O/A ratio 1.75). 61

Figure 4.11 – Ni extractions vs. contact times (Aliquat336 concentration 0.305 M and O/A ratio 1.75). 61

Figure 4.12 – Mo extractions vs. contact times (Aliquat336 concentration 0.305 M and O/A ratio 1.75). 62

Figure 4.13 – Change of extraction efficiency for Co with change in Alamine308 concentration (O/A ratio 1.75 ml/ml and contact time 65 min). 65

Figure 4.14 – Change of extraction efficiency for Ni with change in Alamine308 concentration (O/A ratio 1.75 ml/ml and contact time 65 min). 66

Figure 4.15 – Change of extraction efficiency for Mo with change in Alamine308 concentration (O/A ratio 1.75 ml/ml and contact time 65 min). 66

Figure 4.16 – Effect of O/A ratio on Co extraction (Alamine308 concentration 0.305 M and contact time 65 min). 67

Figure 4.17 – Effect of O/A ratios on Ni extractions (Alamine308 concentration 0.305 M and contact time 65 min). 68

Figure 4.18 – Effect of O/A ratios on Mo extractions (Alamine308 concentration 0.305 M and contact time 65 min). 68

Figure 4.19 – Co extractions vs. contact times (Alamine308 concentration 0.305 M and O/A ratio 1.75 ml/ml). 69

Figure 4.20 – Ni extractions vs. contact times (Alamine308 concentration 0.305 M and O/A ratio 1.75 ml/ml). 70

Figure 4.21 – Mo extractions vs. contact times (Alamine308 concentration 0.305 M and O/A ratio 1.75 ml/ml). 70

Figure 4.22 – Change of extraction efficiency for Co with change in Alamine336 concentration (O/A ratio 1.75 ml/ml and contact time 65 min). 73

Figure 4.23 – Change of extraction efficiency for Ni with change in Alamine336 concentration (O/A ratio 1.75 ml/ml and contact time 65 min). 74

Figure 4.24 – Change of extraction efficiency for Mo with change in Alamine336 concentration (O/A ratio 1.75 ml/ml and contact time 65 min). 74

Figure 4.25 – Effect of O/A ratios on Co extractions (Alamine336 concentration 0.305 M and contact time 65 min). 75

Figure 4.26 – Effect of O/A ratios on Ni extractions (Alamine336 concentration 0.305 M and contact time 65 min). 76

Figure 4.27 – Effect of O/A ratios on Mo extractions (Alamine336 concentration 0.305 M and contact time 65 min). 76

Figure 4.28 – Co extractions vs. contact times (Alamine336 concentration 0.305 M and O/A ratio 1.75 ml/ml). 77

Figure 4.29 – Ni extractions vs. contact times (Alamine336 concentration 0.305 M and O/A ratio 1.75 ml/ml). 78

Figure 4.30 – Mo extractions vs. contact times (Alamine336 concentration 0.305 M and O/A ratio 1.75 ml/ml). 78

List of Symbols and Abbreviations

2FI	Two-Factor Interaction
AMD	Acid Mine Drainage
ANOVA	Analysis of Variance
CCD	Central Composite Design
DF	Degree of Freedom
EDX	Energy Dispersive X-ray spectroscopy (EDX)
CEPA	Canadian Environment Protection Act
HDS	Hydrodesulphurization
HPC	Hydroprocessing Catalyst
HSW	Hazardous Solid Waste
HYD	Hydrogenation
ICP-OES	Induced Coupled Plasma Optical Emission Spectroscopy
M	Molar concentration (mol dm^{-3})
MMSB	Multi Materials Stewardship Board
MSDS	Material Safety Data Sheet
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
SX	Solvent Extraction
TPO	Temperature-Programmed Oxidation
TOS	Time On Stream
USEPA	United States Environmental Protection Agency

Chapter 1: Introduction

1.1 Background and Motivation

In petroleum refining operations, spent catalysts are generated as hazardous solid wastes which can pose a significant environmental impact. The environmental risks associated with these wastes are due largely to the presence of hazardous metals in the spent catalysts such as Co, Ni and Mo. Disposal of these wastes without proper treatment is strongly prohibited by different environmental protection agencies and thus, suitable treatments are required to treat the spent catalysts before being discharged to the environment.

Hydroprocessing catalysts (HPCs) are widely employed in petroleum hydrotreatment operations to remove the sulfur and thus purify the stream, crack the heavier hydrocarbons, and to increase the efficiency of the process. Increased employment of fresh HPCs in petroleum refineries is needed to meet the increased demand for fuels as well as increased production of heavier crude oils and have led to the increased global amounts of generated spent HPCs.

Generally, the management of the spent HPCs differs depending on the volume of the generated waste as well as the local, provincial and national regulations. In many cases, these spent HPCs are discharged into the landfill with continuous monitoring to prevent any negative impacts on the environment. Since there are strict environmental regulations involved with spent HPCs and the rate of their production is also increasing, research on different treatments on waste spent HPCs has been conducted by different investigators. These treatments include, but are not limited to chlorination, leaching, hydrometallurgical

techniques, and biosorption. All of these techniques have their own advantages and disadvantages which will be presented later in the thesis; however, solvent extraction processes have been proposed to be efficient methods for hazardous metals recovery. Despite various investigations, there is still room for improvement as solvent extraction processes sometimes lack cost-effectiveness and may require high reagent concentrations or high contact times for the efficient removal of hazardous metals from spent HPCs. There are several obstacles which should be overcome if solvent extraction is to be employed as an efficient, cost-effective and environmentally-friendly treatment technique. Therefore, increasing the efficiency and cost-effectiveness as well as reducing the environmental risks of such a process has been the focus of the research described herein.

The current study therefore focuses on the solvent extraction process to remove selected hazardous metals from spent HPCs and is the result of a project proposed by the authors for the 2012-13 Leslie Harris Centre MMSB Waste Applied Research Fund, with the collaboration of North Atlantic Refinery Limited in Come By Chance, Newfoundland and Labrador. The spent HPCs employed in this study came from the North Atlantic Refinery Limited. Since there is no treatment plant in Newfoundland and Labrador to treat the waste produced in the refinery, this research provides a great opportunity to investigate the possibility of being able to provide a methodology to remove hazardous metals from spent HPCs in a cost-effective and environmentally-friendly process both locally, and potentially globally.

1.2 Problem statement

Solvent extraction processes are typically not considered to be the most cost-effective methods. Many such processes require a high concentration of extractants as well as long contact times to remove hazardous metals from secondary materials. There is currently much research being conducted globally on different levels to achieve a common goal towards overcoming those challenges and making solvent extraction processes potentially more economical.

One way to make the solvent extraction more economical is to identify an extractant which can successfully remove the hazardous metals from an aqueous phase using a low extractant concentration. Another option toward cost-effectiveness is to reduce the operation time which means the lowest contact time required between the organic and aqueous phase in a solvent extraction process. Increased efficiency is also a key factor in reducing costs and this can be accomplished by achieving the largest possible recovery of the hazardous metals.

The current study focused on: (a) identifying the best leaching agent for dissolution of spent HPCs into an aqueous solution; (b) the improvement of the solvent extraction process to identify a suitable extractant with low required contact time, and low required extractant concentration. Two amine-based extractants (Alamine308 and Alamine336) and a quaternary ammonium salt (Aliquat336) were employed to remove the hazardous metals (Co, Ni, and Mo) from the aqueous solutions, obtained from the dissolution of spent HPCs in acid solutions. Identifying the best extractant and optimized contact time, extractant

concentration, and organic:aqueous ratio leads to improvements in the solvent extraction process in both a cost-effective and environmentally-friendly manner.

1.3 Objectives of the research

The main aim of the current study was to investigate the possibility of using a solvent extraction process using three extractants as a cost-effective and environmentally-friendly process to treat the spent HPCs. Specific Research objectives of our study can also be listed as follows:

- Characterization of the generated spent HPC used at the North Atlantic Refinery Ltd. in Come By Chance, Newfoundland and Labrador.
- Characterization of the acidic leachate before and after solvent extraction using ICP-OES.
- Identifying the most efficient leaching agent to dissolve the metals from the spent catalyst among the three applied concentrated acidic solutions (HNO_3, HCl, and aqua regia).
- Identifying the most significant factors affecting the solvent extraction process, namely contact times, extractant concentrations and organic:aqueous ratios.
- Development of a solvent extraction procedure using Alamine308, Alamine336 and Aliquat336 to remove Co, Ni, and Mo from the generated spent catalyst used by the North Atlantic Refinery Ltd. in Come By Chance, Newfoundland and Labrador.

- Selection of the best reagent for Co, Ni, and Mo extraction based on three factors considered to be the most significant.
- Optimization of the metal extraction process using the Design Expert® software (Design Expert® software, Version 9.0.6; Stat ease Inc., 2015).

1.4 Approach

An in-depth analysis of the solvent extraction basics, its limitations and a thorough investigation on how to improve the process were all conducted in the initial stages of this study. Analysis of the spent catalyst was completed subsequently to achieve a thorough understanding of the catalyst composition.

The experimental stage started with the dissolution of the spent catalyst powder into three different acid solutions (HNO_3, HCl, and aqua regia) and determining the best leaching agent based on the ICP-OES results of the resulting leachates from these acids.

Significant parameters and their levels for the solvent extraction process were identified based upon a literature review of previous studies on solvent extraction of valuable or hazardous metals. Experiments for the solvent extraction process were designed based on the three significant parameters, namely, contact time, extractant concentration, and organic:aqueous ratios, determined using Design Expert® software.

Results of the solvent extraction process were based upon the obtained ICP-OES analyses and the effects of each parameter on the performance of the three extractants used were also determined. The validity of the results obtained were determined using statistical analyses obtained with the help of the software. Optimization was also completed using the

Design Expert® software and optimized points for maximum hazardous metal recovery and minimum contact times were determined.

It should also be noted that research for hazardous metal recovery from secondary materials such as spent HPCs is ongoing and further investigations on the technical, economical, and social implications are required to improve the process' cost-effectiveness and environmentally-friendliness.

1.5 Outline of the thesis

This thesis is divided into five chapters. Chapter 1, entitled "Introduction", presents the background and motivation, objectives, and the approach to the problem used in this study. The current state of the research on metal extraction from spent catalysts is reported in the second chapter entitled "Literature Review". The basics of the spent catalysts, their composition, production, deactivation, regeneration, adverse environmental impacts, and disposal regulations are reviewed in Chapter 2. Treatment methods, their limitations, and areas of improvements are also discussed in Chapter 2. In the third chapter, entitled "Materials and Methods", the materials and the experimental and analytical procedures are all described in detail. Chapter 4 presents the results and discussion on the obtained results. The effects of three significant parameters on each extractant's performance are illustrated and the efficiency of the extractants are compared for the removal of hazardous metals. Chapter 5 contains the conclusions of this study and new perspectives and recommendations for future studies are also proposed.

Chapter 2: Literature Review

2.1 Overview

In this chapter, HPCs and their compositions are described in detail, and their deactivation and regeneration processes are explained. Disposal restrictions and a few relevant pollution prevention techniques are also discussed. At the end of the chapter, treatment options such as hydrometallurgical, chlorination, and biosorption techniques are described and evaluated.

2.2 HPCs

2.2.1 Usage in petrochemical industries

As described in Chapter 1, HPCs are widely used in the petrochemical industry, mostly to purify the hydrocarbon processing streams. These catalysts are mainly employed to enhance the efficiency of the process, to remove sulphur from the stream, and to break-down the heavier hydrocarbons into short-chain sulphur-free hydrocarbons (Ancheyta and Speight, 2007). Spent HPCs are classified as hazardous solid wastes (HSWs) produced in petrochemical industries, according to both the United States Environmental Protection Agency (USEPA) and the Canadian Environmental Protection Act (CEPA) due to the presence of hazardous materials including, but not limited to, heavy metals, metal oxides, and metal sulphides (USEPA, 2003). HPCs have very high porosities and surface areas, in which coke can be deposited, causing deactivation of the catalyst. Different sizes and shapes of HPCs have been developed to enhance the catalyst activity and improve the reactor performance and have been described as “sphere”, “pellet”, “cylinder”, “bilobular”,

"trilobular" and "tetralobular" (Furimsky, 2008). The shape and size of the HPCs are especially important when an in-situ regeneration of the reactor after the catalyst deactivation is considered (Furimsky, 2008).

Recently, the use of HPCs has been drastically increasing due to the strict regulations on mandatory sulphur-free or ultra-low sulphur contents in petroleum products such as diesel and jet fuels (Marafi and Stanislaus, 2008). For instance, the maximum sulphur content in on-road diesel fuel is 10-15 ppm (Marafi et al., 2010). All indications suggest that the production and usage of HPCs are going to increase and the market demand for these catalysts is estimated to grow at an annual rate of 4.4% (Silvy, 2004). The market for fresh hydrotreatment catalysts is currently around 120,000 tons per year. It has been declared that 50% of this amount (60,000 tons per year) are employed for cleaning the fuels produced as column distillates, and the remaining 50% are used to upgrade and purify the residues. The same trend is expected for the hydrocracking catalyst market, which is currently around 10,000 tons per year and is expected to grow at a rate of about 5% per year (Marafi and Stanislaus, 2008).

The increasing rate in fresh catalyst usage is the most significant factor for the increase of the discarded spent catalysts; however, there are many other factors upon which the total volume of spent HPCs discarded as solid waste depends. These parameters include, but are not limited to:

- Increasing need for fresh catalysts in hydroprocessing units to meet the increasing demand for production of ultra-low sulfur-containing fuels.

- Reduced cycle times due to severe operational conditions in diesel hydrotreating units.
- A constant growth in the distillation processing of heavier feed streams with much higher sulfur and metal contents.
- Reduced catalyst deactivation times due to faster deactivation rate and unavailability of reactivation processes for residue HPCs.

The mass of spent catalysts discarded from the hydroprocessing units is always higher than that of the fresh catalyst amounts employed in that unit, due to the formation of coke and metal deposits on the catalyst surface (Nejad, 2012). These metal complexes and the metals present in the fresh catalysts in the first place, are both potential environmental hazards and are subject to the environmental regulations.

2.2.2 Composition of HPCs

The composition of the HPCs depends largely on the type of catalysts and their supports used for a specific product stream (Marafi et al., 2010). The composition of the catalysts employed for light and heavy feedstock are quite different. Light feeds do not usually contain metals and asphaltenes, and the catalyst composition is very critical in these situations. The choice of the catalyst and its composition should be based on the type and content of sulphur and nitrogen heteroatoms. For heavier feedstocks containing high concentrations of heavy metals and asphaltenes, the physical properties of the catalyst are much more important than the catalyst chemical composition, as the shape, size, and porosity of the catalysts are critical factors to achieve the full utilization of the catalyst. In

some cases, different modifications may be necessary, depending on the type of the feedstock.

To date, various catalysts containing different types of metal complexes have been developed for hydroprocessing purposes. The Mo/W-containing supported catalysts, are typically "promoted" by Co and Ni, and have been employed in hydroprocessing units for decades. "Promotion" is defined as the action of a few substances in small quantities, also called promoters, to improve the activity, selectivity, stability, and/or accessibility of the catalyst for specific reactions (Vayenas, 2001; Rothenberg, 2008).

The predominant catalyst support for hydroprocessing processes has been γ-Al_2O_3; however, other supports have also been used, such as silica-alumina, zeolites, Al_2O_3-TiO_2, and TiO_2, to increase the catalyst activity and enhance its performance. In $CoMo/Al_2O_3$ catalysts, several species can be found on the catalyst surface such as MoS_2, Co_9S_8, and Co/Al_2O_3 (Topsøe et al., 1996). It should also be considered that the metals and metal complexes contained in spent HPCs not only depend on the synthesis of the fresh catalysts, but also largely depend on the feedstock composition and its heavy metals contamination (Furimsky, 2007).

2.3 Deactivation and regeneration of HPCs

HPCs are used in various petrochemical processes such as hydrogenation (HYD), hydrodesulphurization (HDS), hydrocracking (breaking the C-C bonds), and many more catalytic processes. Hydrocracking catalysts mostly contain a Mo support on alumina as a typical carrier, and are promoted by Ni and Co. Hydroprocessing reactions take place on

the active metal sites on the sulphur vacancies located on the edge of the MoS_2 crystallites. These vacancies are much more active when promoted by Co and Ni as well (Ancheyta and Speight, 2007).

Deactivation of HPCs is defined by the decline in the rate of hydroprocessing reactions with time-on-stream (TOS), and usually occurs when a strongly adsorbed molecule occupies an active vacancy. These molecules can be nitrogen-containing compounds, coke molecules, metals, and other basic molecules. Normally, deactivation takes place by multiple causes, to different degrees. These causes can be defined as active site blockage by strongly adsorbed species, active site coverage by coke or different metals, and/or sintering at high temperatures. Some of these causes and their significance on catalyst deactivation for three typical hydroprocessing processes are listed in Table 2.1 (Ancheyta and Speight, 2007). Deactivation is generally dependant on catalyst structure, operating conditions, and also feedstock characterization. (Marafi et al., 2010; Furimsky and Massoth, 1999). For instance, during processing of light feeds, minimal deactivation occurs, while heavier hydrocarbons cause severe and rapid deactivation of the catalysts and therefore reduce the lifetime of the HPCs (Furimsky and Massoth, 1999).

Table 2.1 Relative effects of coke and metals deposition on the deactivation of HPCs in three typical reactions (Ancheyta and Speight, 2007).

Catalyst function	**Relative effect**	
	Metals	**Coke**
Hydrodesulphurization (HDS)	Moderate	Moderate
Hydrogenation (HYD)	Weak	Strong
Hydrocracking (breaking C-C bonds)	Weak	Very strong

Different types of deactivation may occur to different degrees depending on the characteristics and compositions of the feedstock and usually follow the S-shaped curve of temperature vs. time-on-stream, as illustrated in Figure 2.1 (*top*). This trend shows that the activity decline rate can be offset by increasing the temperature. The typical deactivation curve for activity loss vs. time is also shown in Figure 2.1 (*bottom*). Initially, coke deposition and adsorption of poisons can dominate catalyst deactivation for a heavy feedstock, which can cause a rapid deactivation of the catalyst over several days. At this point, little contribution of metals to the overall catalyst activity loss may be observed. Deactivation by metal deposits usually occurs during a much longer period of almost stable activity (mostly linear increases with time on stream), until drastic deactivation occurs which is typically caused by pore restriction, sintering, and/or blockage of the pore structure at the end of the run (Ancheyta and Speight, 2007; Vogelaar, 2005). When metals are deposited on the catalyst surface, they affect the permeability of the catalyst. For example, V and Ni are gradually converted to their sulphides. Permeability and metal deposition have adverse effects on each other, as metal deposition increases, permeability is reduced, and catalyst activity diminishes.

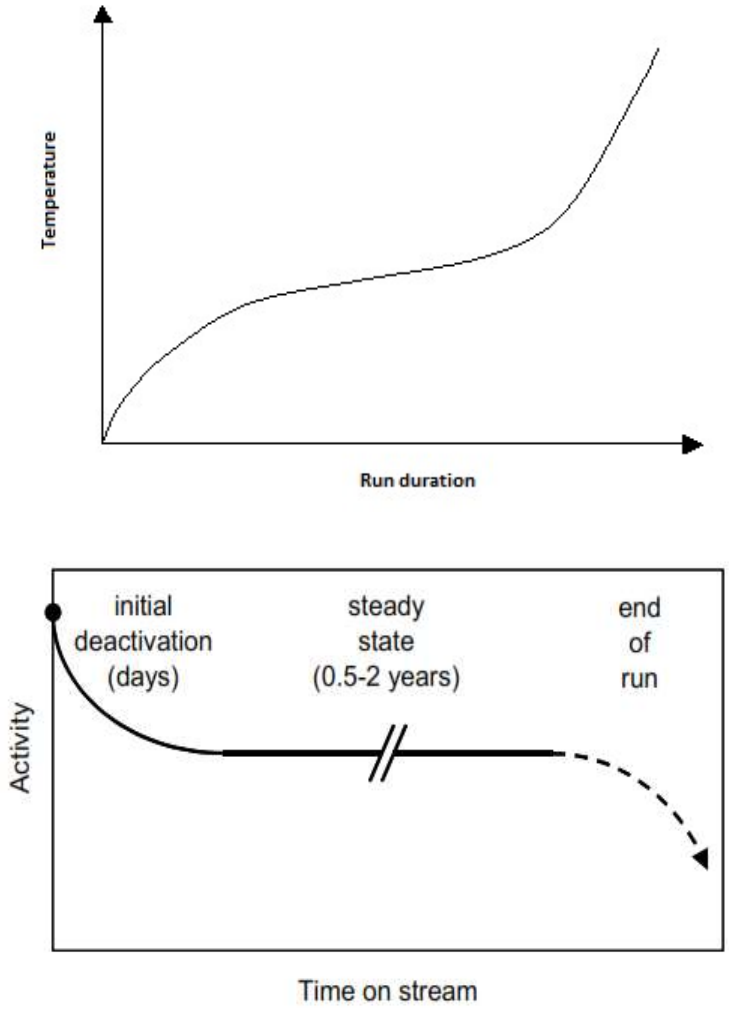

Figure 2.1 Typical S-shaped catalyst deactivation curve (*top*) (Ancheyta and Speight, 2007), and typical activity loss curve for an HPC vs. time on stream (*bottom*) (Vogelaar, 2005).

During hydroprocessing of light feedstock, the catalyst can last for several years in operation; however, prolonged exposure to high operating temperatures can cause catalyst recrystallization which modifies the porosity and surface area (Marafi et al., 2010). For distillate feeds, coke deposition and poisoning with nitrogen-containing compounds are the most significant factors causing catalyst deactivation, sometimes occurring in parallel. As

the boiling range of the feed increases, coke deposition on the catalyst active sites increases as well. For nitrogen-containing compounds, their strong adsorption at the active sites on the surface of the catalyst can cause deactivation. As the feedstock becomes heavier and the contained metals and asphaltenes increase, the coke deposition usually increases. The amounts of coke deposited on the catalyst active sites is governed by the feedstock resins and asphaltenes, as shown in Figure 2.2 (Furimsky, 2007).

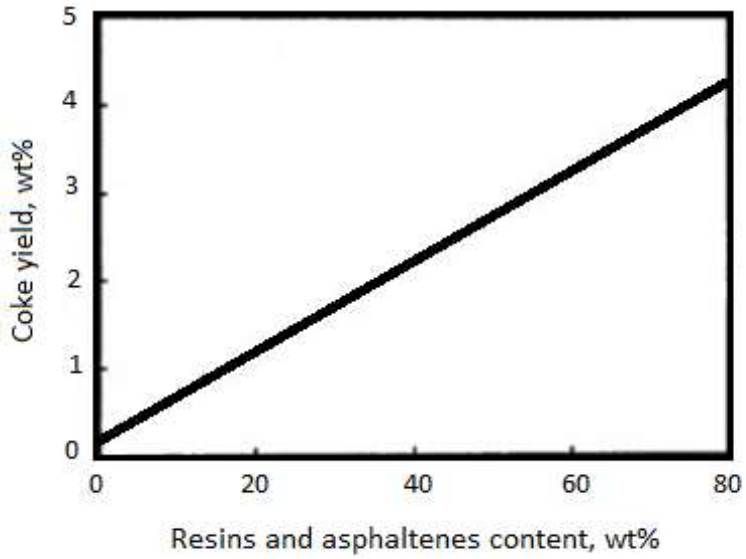

Figure 2.2 Deposited coke on HPCs as a function of the content of resins and asphaltenes according to three experimental samples for $NiMo/Al_2O_3$ catalysts at 8.5 MPa of H_2 and 673 K (Furimsky, 2007).

2.3.1 Extending the lifecycle of HPCs

Research and development is a key factor toward the synthesis of improved HPCs. This requires a clear and deep understanding of the catalyst key properties such as the nature of the active sites and their structure, the textural characteristics of catalyst supports (alumina,

carbon-supported, etc.), and pore size distribution and its significant influence on the catalyst's performance.

Different methods have been proposed to extend the lifecycle time of HPCs. A recently patented method has however been developed which successfully increases the life-times of these catalysts. The "React Technology" was introduced in 2003 by Albemarle and Nippon-Ketjen to restore the performance of spent HPCs to close to their original levels (Hoffman and Leliveld, 2013). Currently, more than 150 customers worldwide are using this patented method in more than 750 petrochemical units (Hoffman and Leliveld, 2013). React Technology uses a proprietary regeneration process which is then followed by re-dispersion of the active metals on the catalyst surface. For HPCs, the active sites are re-created and are protected by an organic coating. The React Technology treatment is capable of improving catalyst performance, and also enhancing the activity of the catalyst, up to typically 95% of its initial value (Hoffman and Leliveld, 2013).

2.3.2 Regeneration of HPCs

When a catalyst is deactivated, its activity decreases, and its performance drops. Deactivation also causes poor catalyst stability and decreased conversion rate with time (Ancheyta and Speight, 2007). The first action required in order to achieve the minimum conversion rate required for an efficient process when deactivation occurs is to gradually increase the temperature of the catalyst bed. After some time, this method is no longer effective due to severe coke formation and undesirable product yields as well as increased cost. Deposited coke can be of the soft or hard (refractory surface coke) types which are

adsorbed weakly and strongly onto the active sites of the catalyst, respectively (Ancheyta and Speight, 2007). Temperature-programmed oxidation (TPO) can help for the analysis of the type of the produced coke.

As the catalyst activity goes below the minimum value required for the process, the first choice is to regenerate the catalyst, since disposal and/or landfilling should be considered as the last option. The regeneration process usually includes burning off the carbonaceous deposits by oxygen and inert gases under controlled temperatures (Ancheyta and Speight, 2007). Uncontrolled temperatures may lead to recrystallization and/or sintering of the catalytic active sites (Furimsky, 2007).

Complete regeneration of the catalyst is very difficult to achieve and is practically impossible; however, 80% recovery of the fresh catalyst activity is required for the regeneration process to be considered desirable (Furimsky, 2007). In most cases, there are metal sulphides and other metal complexes on the catalyst active sites which cannot be burned off completely. In general, poisoning by metal deposition is irreversible, and vanadium and nickel oxides for example, may also be left on the surface of the catalyst after regeneration. It is possible to eliminate the metal deposits from the surface of the catalyst by mild chemical methods such as leaching (using not very strong acids) without destroying the support and avoiding excess removal of Mo (Ancheyta and Speight, 2007).

Another problem, which may occur during oxidative regeneration processes, is the sintering and redistribution of the active metallic phase of the catalyst with the consequent loss of the catalyst's active sites. In order to restore the maximum catalytic activity possible in the regeneration process, careful handling of the catalyst, control of the regeneration

temperature and gas composition such as oxygen and nitrogen are significant factors to consider (Ancheyta and Speight, 2007).

Another option for the recovery of the deactivated catalyst's activity is reductive regeneration. In this case, at the end of the operation, the feed streams are discontinued, while continuing the H_2 supply. There is far less information on reductive regeneration of HPCs which may be due to the fact that, in most cases, oxidative regeneration has been the most effective option for catalyst activity restoration. Even at very high temperatures, reductive regeneration cannot compete with oxidative regeneration for activity restoration (Furimsky, 2007). Other regeneration processes such as regeneration with H_2O, CO_2, and NO_x have also been suggested in the published literature but are not as effective and well-known as oxidative regeneration, and are described by Marafi (Marafi et al., 2010).

2.4 Environmental aspects of spent HPCs

As previously described, production of HPCs has been on the increase requiring increased production of metals from their ores obtained from mining operations. The extraction of these metals such as Co, Mo, V, and especially Ni has had several adverse effects on the environment such as increased acid mine drainage (AMD) at mining sites. On the contrary, use of HPCs in sulphur removing processes in petrochemical industries has several advantages to the environment. The most significant advantage is the reduction in the amount of sulphur present in produced fuel product such as diesel or jet fuels. Combustion of these petroleum refinery products produces hazardous gases and, if the sulphur is present in higher amounts, significant amounts of toxic SO_x gases will be produced. Efficient

operation of HPCs can reduce the amounts of SO_x gases released into the environment. Disposal of solid waste HPCs, however, causes serious challenges for researchers in industry and academia as these hazardous wastes cannot be released into landfills without proper treatment(s) (USEPA, 2003). Landfilling is the last option to consider and all efforts must be made to minimize spent HPCs in landfills (Marafi et al., 2010). Different areas should be reviewed before treatment method selection such as the hazardous nature of the spent HPCs, how they are contaminated, how to handle these solid wastes, their life cycle assessment, and pollution prevention techniques.

2.4.1 Disposal regulations

There are several strict regulations regarding the disposal and/or landfilling of spent HPCs, as they are considered hazardous solid wastes produced in petrochemical industries by the USEPA (USEPA, 2003). These regulations include, but are not limited to (directly quoted) (Hoffman and Leliveld, 2013) the following:

- No waste may be exported to any Third World countries having inadequate facilities.
- No waste may be taken to a facility that is not properly equipped to recycle hazardous solid wastes.
- The country, state, and/or the province, where waste requiring treatment is generated, is responsible for its treatment.
- Hazardous waste for recycling may be shipped to authorized facilities anywhere in the world, but only under a highly regulated system.

For spent HPCs, recycling may involve shipment of wastes to a company capable of regenerating spent catalysts for reuse. However, when HPCs are deactivated and can no longer be regenerated, they should be treated properly before disposal. Landfilling or disposal of these hazardous materials are strongly prohibited by environmental authorities. There are several hazardous metals present in the spent HPCs which are responsible for their toxicity, and which should be removed by efficient, easy-to-implement, and environmentally-friendly processes before catalyst disposal and/or landfilling.

2.4.2 Catalyst contamination

After the catalysts are deactivated and can no longer be regenerated, they are considered to be spent catalysts which are environmental hazards, as there are various contaminants on their surfaces which can be leached into the environment. These contaminants can originate from different sources such as the feedstock (mainly V, Ni, As and Na), or from additives employed in refining operations (silicon, lead), or from corrosion (iron), (Dufresne, 2007).

Ni and V, if present in feedstocks, are included in larger-size molecules (with boiling points >500 °C) in the heavier fraction of vacuum gas oil (VGO). These metals are present in higher concentrations in heavy oils and bitumen than in conventional oils; however, the exact composition of these metals is still a point of contention among scientists in the field (Dechaine and Gray, 2010).

These larger Ni and V containing molecules can easily be decomposed at the Ni and V sulphide active sites on the surface of the catalyst. However, it is more difficult to regenerate deactivated catalysts contaminated with vanadium due to their ultra-low activity,

and reuse or regeneration of the catalysts are not recommended when they have become deactivated with more than 1-3 wt. % vanadium (Dufresne, 2007).

Arsenic compounds may also be present as a contaminating material in many crude oils. Predominant arsenic compounds in various crude oils are the aryl- and alkyl-partially oxygenated arsines (Ovchinnikov et al., 2013). If present, there is usually a sharp steep arsenic gradient between the top and the bottom of the fixed-bed reactor, as the arsenic compounds are extremely reactive under the conditions of hydroprocessing and thus are easily decomposed and adsorbed on the surface of the catalyst. They become decomposed at the first stages but usually not beyond that. Arsenic is a serious and significant poison to the catalyst and can deactivate a HPC at very low concentrations of only 0.2-0.4 wt. % (Dufresne, 2007).

Other metals can also be considered as serious contaminants. For example, sodium can be present in spent HPCs if caustic soda is introduced in upstream operations. Another example is silicon in the feedstock, which can originate from different foaming agents, added to the lighter fractions of coker or visbreaker operations. Contamination with iron resulting from corrosion of upstream equipment can also occur.

When a catalyst is deactivated and cannot be regenerated, the amount of each contaminant such as vanadium, cadmium, arsenic, and nickel should be measured and compared to the respective environmental regulations such as USEPA or CEPA for disposal and/or landfilling. These solid waste spent catalysts should also undergo proper treatment(s) before their disposal into the environment (USEPA, 2003).

2.4.3 Handling of spent HPCs

In many cases, when the catalyst performance decreases, the decline in catalyst activity can be offset by adjustment of some operating parameters (e.g. temperature). When this method is not capable of restoring the catalyst activity, the reactor operation has to be discontinued. The reason for this can be a high pressure drop caused either by solid accumulation on the front of the fixed bed due to the attrition of catalyst particles and formation of clumps, or catalyst sintering which is caused by high temperatures. In most cases, catalysts have to be removed from the fixed bed reactor, which then should be reloaded with either a fresh or a regenerated catalyst. Many fixed bed reactors employed in hydroprocessing units are equipped with nozzles, specified for dumping the catalysts into a receiving container, as illustrated in Figure 2.3 (Volesky, 1990). In a few situations, refinery companies apply their own specific procedures; however, in most cases, in order to withdraw the spent HPCs, the nozzle is opened under a purge of nitrogen (N_2). Dry ice (CO_2) is also added to the filled containers to expel the remaining air. The removal of the remaining amounts of HPCs may require personnel to enter the reactor, taking into consideration all safety regulations, i.e. it is essential that, in such cases, the personnel carry all mandatory safety equipment to prevent any serious harm or injuries.

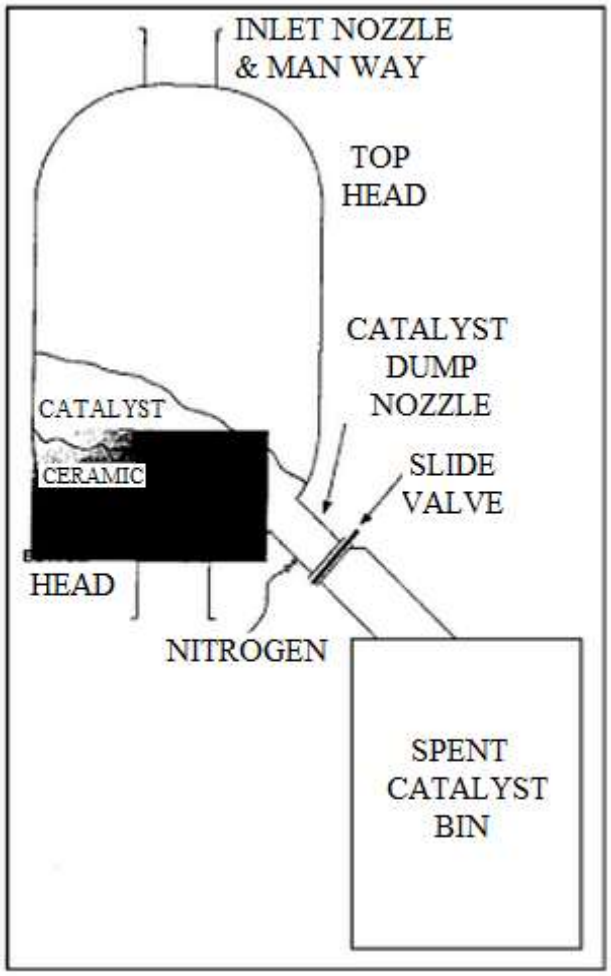

Figure 2.3 The withdrawal system of spent HPCs from fixed bed reactors (Volesky, 1990).

2.4.4 Pollution prevention techniques

Besides extending the lifecycle of catalysts, as previously discussed, many different techniques have been proposed to reduce the pollution effects produced by using HPCs. Many researchers suggest that using alternative catalysts with similar physical and chemical properties and equal efficiencies, but lower levels of toxicity is an excellent option to reduce pollution (source reduction technique). Other techniques provide solutions involving the optimization of the entire sulphur removal process, so that the catalyst will

last longer (increasing product life technique) in new facilities or optimized facilities designed for less harmful environmental impacts.

In general, the quantity of spent HPC discarded as solid waste can be reduced if the useful life of the catalyst before disposal can be extended for a longer period of time. This can be done in three ways (Marafi and Stanislaus, 2008):

- Employing a catalyst with reduced performance in less demanding catalytic processes.
- Regeneration and/or reuse using novel techniques.
- Reducing catalyst consumption by using improved catalysts with longer lifetimes such as, for example, nano-catalysts having larger surface areas and porosity.

2.4.5 From preparation to disposal (cradle-to-grave approach)

The life-cycle of an HPC starts with the initial production of fresh catalyst which is pre-sulfided prior to being employed in the refinery process. A pre-sulfiding process is typically conducted to enhance the activity of fresh or regenerated HPCs (Gaylord Chemical Company, L.L.C., 2007). Figure 2.4 illustrates how the active metals Co and Mo are placed on the alumina support sulfide catalyst. The following flow-chart shown as Figure 2.5 also shows the steps of production, use, and disposal of HPCs.

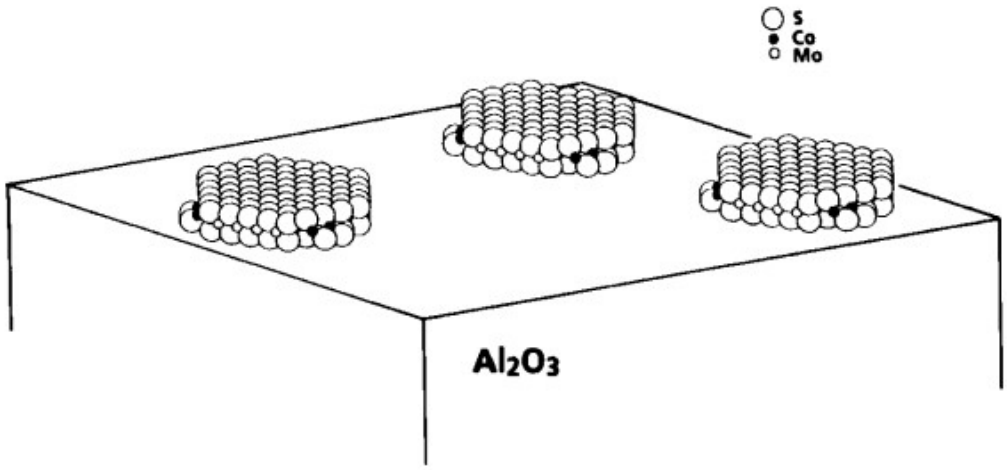

Figure 2.4 Sulfided Co/Mo catalyst on alumina support showing the Co tetrahedrally coordinated at the edge of a single layer of MoS_2 (Occelli and Anthony, 1989).

During its use, the catalyst becomes deactivated mostly due to coke deposition on the catalyst active sites, and/or sintering. When the catalyst becomes deactivated, the catalyst cannot meet the performance targets within the limits of the reactor operating conditions, and thus the reactor is shut down. Depending on the degree and nature of catalyst contamination, it can be either directly regenerated, undergo an additional reactivation treatment, be recycled, or landfilled after proper treatment (Eijsbouts et al., 2008).

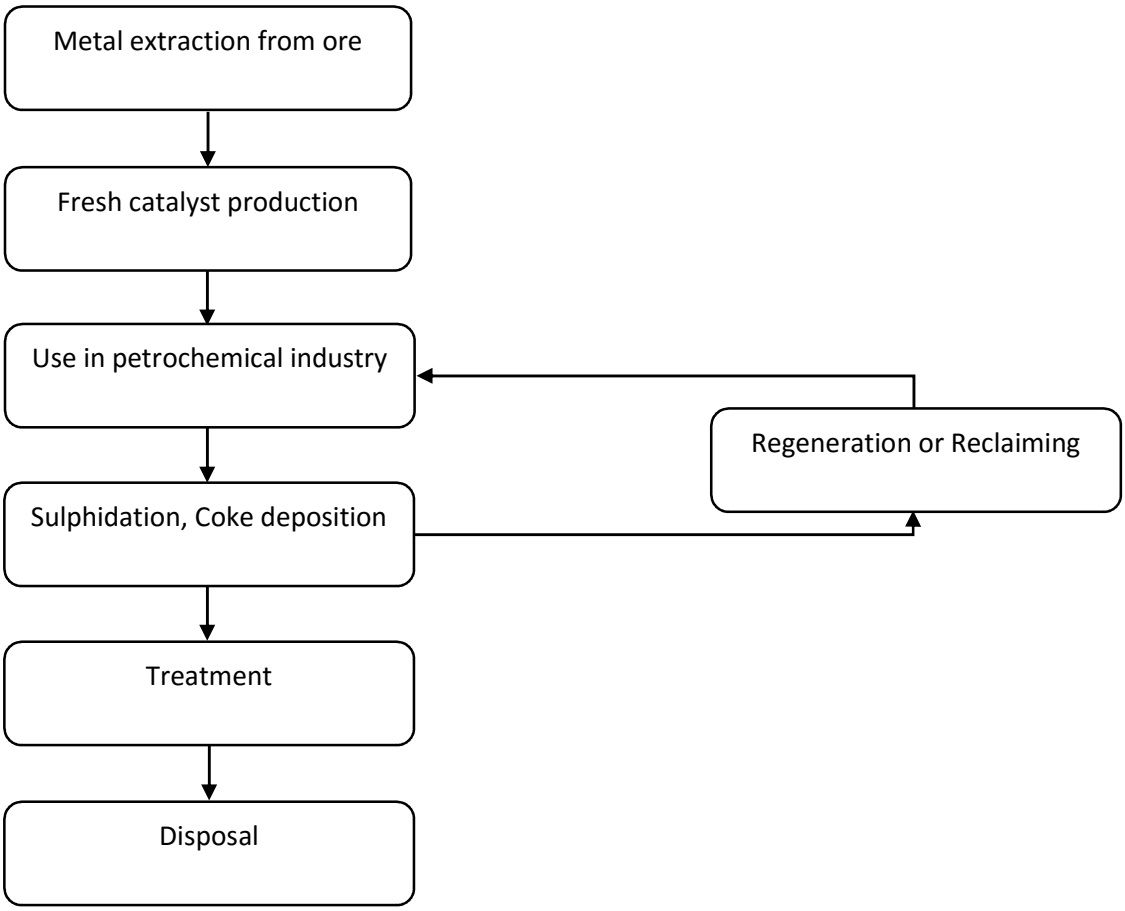

Figure 2.5 Hydroprocessing production to disposal (Eijsbouts et al., 2008).

The regeneration step is a vital step in pollution prevention. The deactivated catalyst can be regenerated several times before it becomes waste. Therefore, optimizing the regeneration processes can be considered a significant technique to prevent pollution and to reduce the impact on the environment by improving the life-time of the HPCs in use (Marafi et al., 2010).

A detailed "cradle-to-grave" approach is also illustrated in Figure 2.6. All of these detailed steps have their own impact on the environment, some being more significant than others. It should also be mandatory that disposal should only be considered when the regeneration

is unsuccessful. Landfilling is also the last step to consider due to the hazard potentially posed to the environment and, as emphasized previously, proper treatment(s) should be developed prior to disposal. In such treatments, the metals should be removed and recovered from the spent catalysts which are not suitable for regeneration. These reclaimed metals from any disposed catalyst can be reused for further catalyst synthesis and thus decrease the need for increased metal mining to produce the required ores (recycle and reuse techniques) (Eijsbouts et al., 2008).

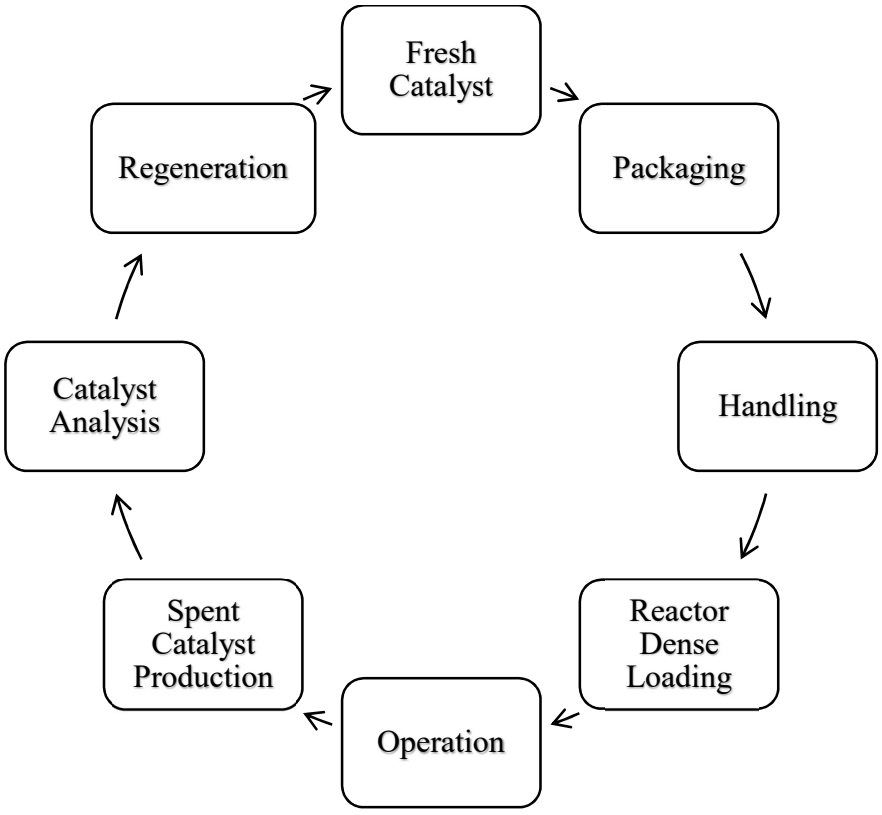

Figure 2.6 The cradle-to-grave approach for HPCs (Eijsbouts et al., 2008).

Typically, the catalyst life-cycle involves a long series of operations, normally performed by different specialized companies. In addition to manufacturing, these operations include transportation, loading, replacement, regeneration, metal reclaiming, supplying different chemicals and materials, and other operations. Different factors, including the multiplicity of steps, the large number of different companies involved as well as technical, logistic and environmental issues involved, all serve to make it imperative to manage the catalyst life-cycle in the most efficient and responsible way possible. Previously, each of the consecutive steps in the life-cycle of the catalyst was typically handled by a different company under the direct coordination of the refinery itself. Recently, however, leading catalyst manufacturers have started to provide "catalyst management'' services to their refinery customers.

2.5 Treatment of spent HPCs (metal removal and recovery)

Metal removal and recovery from spent HPCs can be studied from two different perspectives: (i) environmental, and (ii) economic aspects. As previously described, spent HPCs have been classified as hazardous substances by USEPA definitions and cannot be disposed into the environment or landfilled without proper treatment. From an economic perspective, metals in high concentrations may be isolated from other metals and be recovered for reuse. Studies have shown that, in generic NiMo catalysts used in hydrocracking units (the type of catalyst sample used in the present study), Co, Ni and Mo are usually in the highest metal concentrations in the spent catalyst (Furimsky, 2007). Co is the most significant metal among these three to be considered for environmental issues;

however, Co, Ni and Mo recovery can be studied for economic reasons as well (Banda et al., 2012), especially Mo which is considered a strategic metal (Ghadiri et al., 2014).

Several methods have been proposed for metal separation and recovery from spent HPCs such as chlorination, acid leaching, solvent extraction (hydrometallurgical method), biosorption, and a few other techniques. In the next few sections, the main significant treatment methods are briefly described and advantages, disadvantages, and/or recent advances in each of them are described.

2.5.1 Chlorination

Chlorination is a process in which the metals present in the spent HPCs are transformed into different volatile and non-volatile chlorides and the chlorides are selectively separated using other processes (Marafi et al., 2010). Initially, hydrocarbons and residual oil in the spent HPCs are removed by solvent extraction and then the spent catalyst containing hazardous metals, the alumina support, and coke is treated using gaseous chlorine at high temperatures ranging from 500 – 600 °C. For instance, Mo and Al can be converted to volatile chlorides under similar conditions and be separated using condensation and/or precipitation at controlled pH values (Marafi et al., 2010). V and Ni can also be converted to chlorides by employing agents such as Cl_2, HCl, S_2Cl_2 and CCl_4. Vanadium forms VCl_4 as a volatile chloride, and nickel forms $NiCl_2$ as a non-volatile chloride as well. Vanadium can be recovered from the gas stream by condensation of the VCl_4 and the nickel can be separated as $NiCl_2$ from the solid residue using a solvent extraction process (Marafi et al., 2010; Yoshida et al., 1980).

Although chlorination has been suggested to be an efficient method to remove and separate hazardous metals such as V and Ni from spent hydroprocessing catalysts, high required temperatures and other controlled operating conditions make such a process expensive. Furthermore, the use of chlorine and carbon tetrachloride as the chlorination agents involves significant health and safety concerns and makes the process a risky non-environmentally friendly process.

2.5.2 Leaching

Leaching processes, using different types of leaching agents, have been developed for most of the studies on hazardous metal removal from spent HPCs. The leaching agents proposed differ from simple ammonia and ammonium salts, alkalis, organic and inorganic acids, and microorganisms (bioleaching). Each of these leaching agents have their own advantages and disadvantages which can be found in detail elsewhere (Marafi et al., 2010). For example, the use of organic acids have the advantage of requiring less safety precautions compared to the use of inorganic acids such as hydrochloric and/or sulfuric acids; however, they typically have lower efficiency in leaching all the hazardous metals from the spent HPCs into the aqueous solution. Another example is the bioleaching with microorganisms such as bacteria or fungi which has the advantage of high selectivity and high efficiency; however, bioleaching suffers from high required leaching times and insufficient research having been reported on bioleaching processes.

Significant parameters that can affect a leaching process are the type of the leaching agent, its concentration, leaching time, and the temperature. Figure 2.7 shows a diagram of the

order of processes to follow after the leaching process for hazardous metal removal from spent HPCs on the alumina support, and how leaching is followed by the required solvent extraction processes.

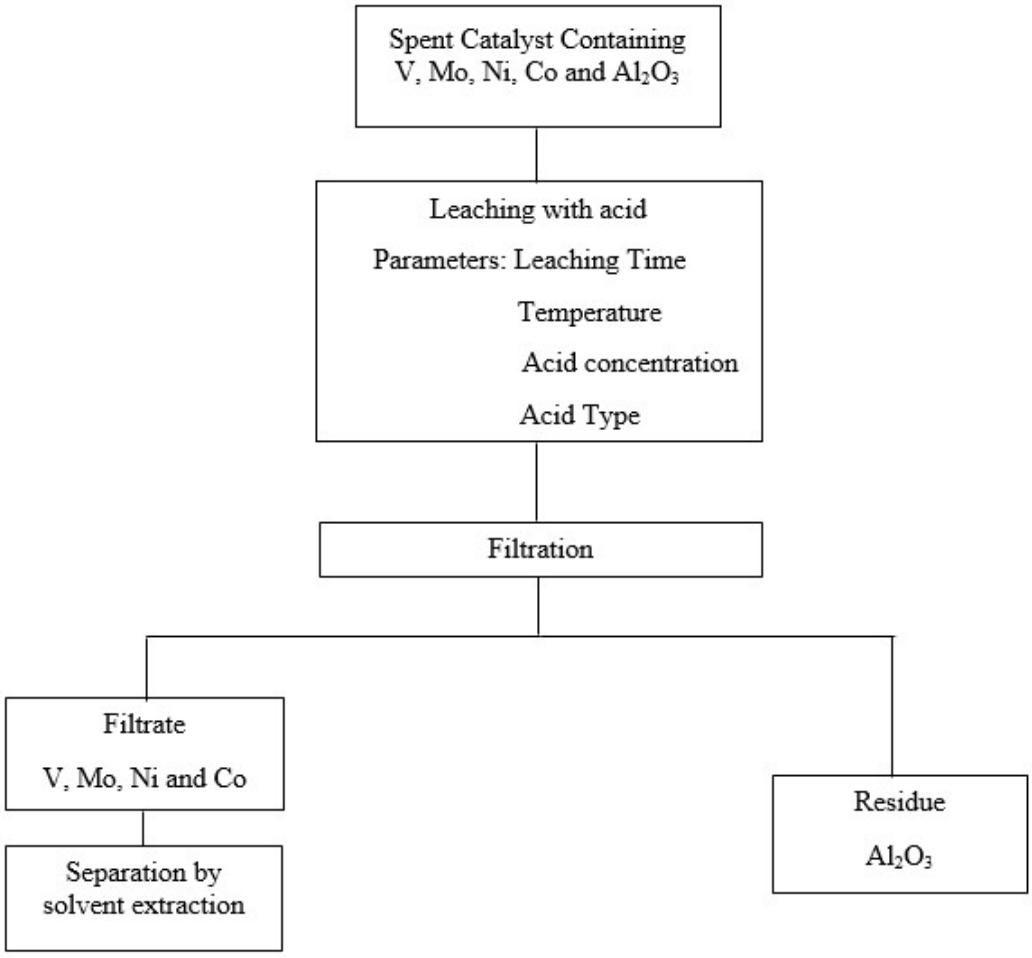

Figure 2.7 Metal extraction using acid (Marafi et al., 2010**).**

When the hazardous metals are efficiently dissolved in the leaching agent, they should be isolated in a pure form using solvent extraction or bisorption methods to selectively separate the metals of interest from other metal complexes.

2.5.3 Biosorption

Biosorption is a fairly new green technology and is defined as the adsorption of hazardous metals onto adsorbents produced from dead biomass or from living organisms. There are two significant advantages of biosorption over conventional methods to remove and recover metals from secondary sources (Volesky, 1990):

- It is an environmentally-friendly process using biomass adsorbents which will not require any organic solvents. Therefore, biosorption reduces the extra pollution which results when hydrometallurgical methods are used.
- It is a very cost-effective method as it employs relatively inexpensive biomass (especially dead biomass) materials to selectively separate the hazardous metals from other secondary sources and/or wastes.

A significant limitation of this method however, is reported to be the slow adsorption of metals. Therefore this has to be overcome for this method to be considered feasible for industrial applications. Furthermore, the only information available in the literature for biosorption is limited to lab-scale batch experiments. Other disadvantages include, but are not limited to, the lack of sufficient knowledge of the mechanism(s) of the adsorption process, insufficient data on possible industrial applications in continuous processes, and the lack of reliable data on the most effective bioadsorbent to use.

2.5.4 Hydrometallurgical processes

Solvent extraction (SX) is a well-known hydrometallurgical technique used in the processing of hazardous metal removal from spent HPCs. Extensive information is

available in the literature for the removal and recovery of metals from different secondary sources using hydrometallurgical methods. In most cases, more than one metal is present in the solution when the secondary material's metals (in this case, spent catalysts' metals) are dissolved in the leaching agent(s). Solvent extraction has been shown to be a feasible and fairly cost-effective method among all hydrometallurgical methods to remove the metals from synthetic and industrial solutions. Various organic solvents which possess high selectivity towards the metal(s) of interest have also been studied for use in such processes. For Co, Ni and Mo, these extractants include, but are not limited to phosphate-based, amine-based, and different Cyanex extractants (Cheng et al., 2010; Hosseini et al., 2012; Banda et al., 2013; Sahu et al., 2013; Fujii et al., 2001; Kumar et al., 2001; Kim et al., 2015; Zeng and Cheng, 2009). When the extraction of the targeted metals is optimized using different extractants, methods such as precipitation under controlled conditions can be used to isolate the metal or metal compound(s) (Furimsky, 2007).

In solvent extraction, the first step is usually to leach the spent HPC in a strongly acidic medium such as HCl, HNO_3, H_2SO_4, or aqua regia. There are several important factors needed to achieve complete dissolution, so the remaining insoluble inert support (usually Al_2O_3) can be discarded as an inert non-hazardous substance. When the leached solution is filtered, an organic solvent employed to extract and selectively isolate the hazardous metals comes into contact with the leachate for a specific amount of time. Figure 2.8 illustrates how a single-stage batch solvent extraction process works.

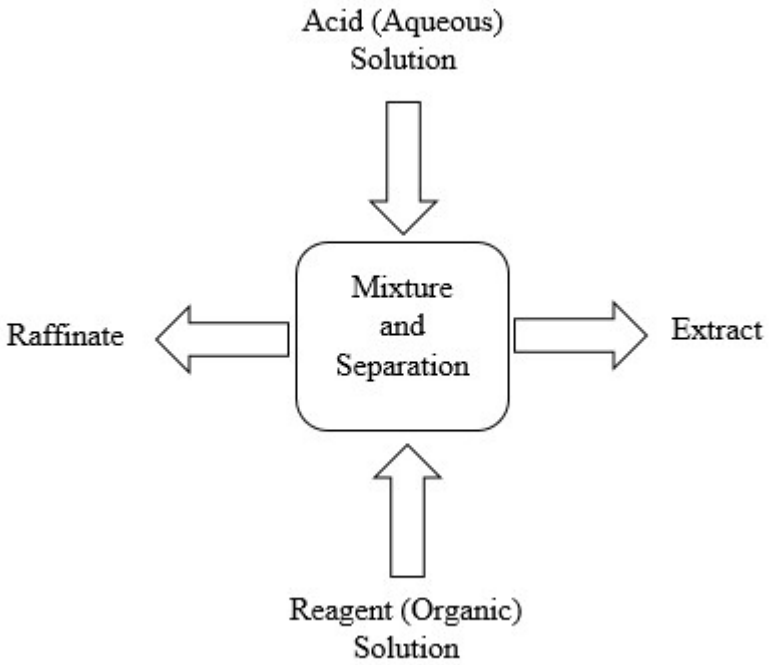

Figure 2.8 Single-stage batch solvent extraction process where an acid (aqueous) solution becomes in contact with an organic phase rich of the extractant.

Although there have been a few investigations on solvent extraction processes for metal removal and separation from secondary materials, there is still plenty of room for improvement. Much of the research results show high required extractant concentration for hazardous metals removal, high required contact times to reach the appropriate extraction efficiencies, as well as the need to use a hazardous substance as the reagent for extraction purposes. On the other hand, elaboration on the behaviour of aqua regia on metal leaching, metal extraction from aqua regia, and a comparison between efficient extractants using the effect of significant factors to be evaluated are all missing from the literature. Furthermore, there has not been much research that has been reported on investigating the statistical

reliability, prediction of hazardous metal removal, and optimization of the solvent extraction processes. Therefore, a need was determined to be undertaken to:

i. Investigate and compare different leaching agents' capabilities to remove hazardous metals from the spent HPCs.
ii. Use different extractants, and compare their extraction efficiencies using significant factors affecting the extraction process.
iii. Develop a mathematical model to predict the behaviour of the extraction process outside of the designed limits.

2.6 Response surface methodology (RSM)

Response surface methodology (RSM) has been widely used as a practical and economical method to optimize different metal extraction, ion-exchange, and hydrometallurgical processes. Three steps are defined in the RSM technique. The first one is to design the experiments to evaluate the effects of different factors on the efficiency of the process. The second one is to develop a polynomial model using the experimental results obtained, and to evaluate the fitted model's suitability by applying a statistical analysis. The last step is to determine the optimum conditions needed to achieve the highest possible efficiencies (Hosseinpour et al., 2011). In most cases, a second-order polynomial model is employed in the RSM. Details of such a model and how the coefficients are determined are listed elsewhere (Mason et al., 2003; Montgomery, 1996).

Central composite design (CCD) (Myers, 1971) is the most popular second-order experimental design in the RSM technique. CCD does not require a large number of

experiments, thus minimizing the time and cost required to carry out the experiments needed. CCD also provides enough information for testing the fitness of the predicted model (Hosseinpour et al., 2011).

As stated above, there has been little research reported on investigating the statistical reliability, prediction of hazardous metal removal, and optimization of solvent extraction processes. Therefore, the aims of the present study were to use RSM and CCD to determine the best leaching agent for dissolution of spent HPCs into an aqueous solution, to help identify an efficient, cost-effective, and environmentally-friendly hydrometallurgical process to remove hazardous metals from the HPC acidic leachates using two amine-based and one quaternary ammonium salt extractant in toluene to develop a polynomial model for the process using significant factors, and to optimize the extraction process.

Chapter 3: Materials and Methods

3.1 Overview

In the current chapter, the materials employed in this study are reported and the analytical protocols are concisely and clearly described. The facilities employed for the different analyses are listed and the procedure used to design the experiments and how the significant factors were involved are also described.

3.2 Apparatus and facilities

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to quantify the trace metals in acidic solutions before and after the extraction process, and was conducted by the ICP-OES lab in the Bruneau Centre for Innovation and Research at Memorial University. Scanning Electron Microscopy (SEM, FEI Quanta 400) and Energy Dispersive X-ray spectroscopy (EDX) analyses were conducted by the SEM lab in the Bruneau Centre for Innovation and Research at Memorial University. SEM and EDX analyses were conducted on the spent catalyst samples to develop a better understanding of the metals present, to obtain a detailed two-dimensional scanned image of the catalyst surface, and to observe different metal availabilities on targeted areas as well as the homogeneous nature of the catalyst. The instrument was employed in the SEM lab in the Bruneau Centre for Innovation and Research at Memorial University. A digital pH meter and an electric conductivity meter were also employed to measure the pH and electrical conductivity of the solutions, respectively.

3.3 Materials

The secondary spent HPCs were obtained in powder form from North Atlantic Refinery Limited's plant in Come by Chance, Newfoundland and Labrador and were analyzed as received. A sample of the spent HPCs which were used in this study is shown in Figure 3.1.

Figure 3.1 Spent HPC in powder form before any treatment, as provided by North Atlantic Refining Limited.

These catalysts were specifically used in the hydrocracking processes for jet fuel and gasoline production to convert long-chain hydrocarbons to short-chain, sulphur-free hydrocarbons. Table 3.1 lists the composition of the spent HPC, provided by the North Atlantic Refining Limited and the metal concentration ranges, obtained from their MSDS.

Table 3.1 Information on solid spent HPC composition obtained from MSDS data as provided by **North Atlantic Refining Limited** (MSDS, 2013).

Ingredients	**Wt. %**
Aluminum Oxide	40 – 90 %
Cobalt Oxide	0.1-1 %
Cobalt Sulfide	0 – 10 %
Petroleum Coke	5 – 40 %
Hydrocarbon Mixture	0 – 20 %
Molybdenum Trioxide	0 – 1 %
Molybdenum Sulfide	0 – 25 %
Nickel Oxide	0.1 – 1.0 %
Nickel Sulfide	0 – 25 %
Phosphorus Pentoxide	0 – 10 %
Silicon Dioxide	0 – 20 %
Sulfur	0 – 15 %

For the leaching experiments and for preparing the aqua regia solutions, ACS grade concentrated hydrochloric acid (36.5-38%) and concentrated nitric acid (68-70%) were used as supplied by ACP, Montreal Quebec, Canada.

The three reagents Aliquat336, Alamine308, and Alamine336 were kindly provided by BASF in Tucson, Arizona, USA, and were used without further purification. The chemical structures of these reagents are illustrated in Figures 3.2 and 3.3. The composition of these

three reagents are provided in Table 3.2. Commercial-grade toluene was used as the diluent for all three extractants, to reach the desired concentrations.

Table 3.2 Composition of Aliquat336, Alamine308, and Alamine336, employed as extractants.

Employed reagent (CAS #)	**Chemical name of Constituent Materials**	**Content W/W %**
Aliquat336 (63393-96-4)	Tri-(C8-10)alkylmethylammonium chlorides	60-100 %
	Octanol-1	3-7 %
	Decanol-1	3-7 %
Alamine308 (25549-16-0)	Triisooctylamine	60 – 100 %
Alamine336 (68814-95-9)	Tri-(C8-10)-alkylamines	100 %

a:

n = 1-3

b:

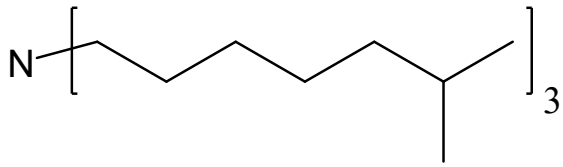

Figure 3.2 General molecular structures of (*a*) tri-N-C8-10-alkyl amines (Alamine336), and (b) triisooctylamine (Alamine308).

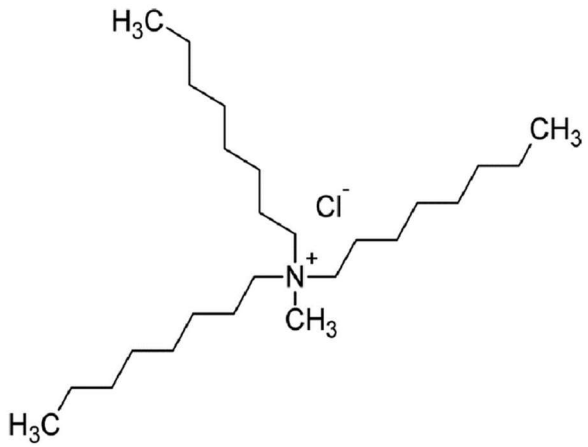

Figure 3.3 Chemical structure of Aliquat336 as its quaternary ammonium chloride salt.

3.4 General experimental procedure

Initially, the spent catalyst sample was roughly mixed to make sure a homogenous sample was achieved before sampling. Quantities of the mixed spent catalyst were dissolved in three different acidic media namely concentrated hydrochloric acid, concentrated nitric acid, and aqua regia to determine leaching efficiency. To obtain a complete dissolution of targeted metals, a solid: liquid ratio of 1:100 (g/ml) was considered and thus, ~ 400 mg samples of spent catalyst samples were each separately dissolved in 40 ml of each of the three different concentrated acid solutions after dissolution for the specified contact times, the acidic leachate mixtures were vacuum filtered through a medium porosity sintered glass Buchner funnel. ICP-OES analysis on the (diluted) acid leachate solutions was conducted and the best leaching medium was selected. Aliquat336, Alamine308, and Alamine336 were employed as the three reagents to extract the hazardous metals from the leachate solutions. Each of these reagents were diluted in toluene to obtain the required concentrations according to the RSM/CCD designed experimental matrix. Different volumes of acidic and organic solutions were then mixed according to the experimental design and were stirred using magnetic stirrers for selected periods of time. Stirring was conducted at a speed at which optimal mixing occurred. The organic phases were separated from the aqueous phases using separatory funnels and the aqueous acidic solutions were analyzed by ICP-OES to determine the metal removal efficiencies according to equations Eq. 1 and Eq. 2 (Nejad et al., 2012; Nejad and Kazemeini, 2012; Nejad et al., 2013) where m represents the specific metal, D is the distribution ratio and C_m is the concentration of the metal in the organic or aqueous solutions. The extraction percentage of the targeted

metals is represented as E%. The distribution ratio of a specific metal D_m is calculated by dividing the metal concentration in the organic phase $[C_m]org$ by its concentration in the aqueous phase $[C_m]aq$. The extraction efficiency E% is also calculated based on the calculated distribution ratio D_m. All experiments were conducted at ambient temperature.

$$D_m = \frac{[C_m]org}{[C_m]aq} \quad \text{Eq. 1}$$

$$E\% = \frac{D_m}{D_m + 1} \quad \text{Eq. 2}$$

The concentration of different metals in the organic phases is measured based on the difference between the ICP-OES results on the aqueous acidic solutions before, and after the extraction of the metals by each of three extractants. Therefore, the extraction efficiencies could be calculated.

3.5 Design of experiments

In the current study, the face-centered central composite design (CCD), the most popular second-order experimental design in the RSM technique, was employed to design the minimum number of experiments required to investigate the effect of different parameters on the extraction of hazardous metals from the spent HPCs, to develop a polynomial model based on the experimental results, and to optimize the extraction process.

Three parameters were considered as being the most significant factors affecting the process efficiency: (i) extractant concentration, (ii) organic:aqueous ratio, and (iii) contact time designated as A, B and C respectively. These factors and their limit values were considered after a preliminary literature review on research conducted on different

hydrometallurgical processes. Table 3.3 lists the minimum and maximum levels for each parameter. Table 3.4 lists the designed experiments using these parameter levels. All three experimental parameters and the designed experiments were the same for all three extractants. Experiments were conducted on the basis of the design matrix of CCD with a full horizontal design method, containing six replicated points. These six-center point replicates, marked in Table 3.4, are the recommended number of center points by the Design Expert software which should not be reduced. Whereas a central composite is typically centered around the likely optimum, more runs at the center levels provide better predictions in the respective areas. Furthermore, the replicates provide an accurate lack-of-fit test (Design Expert® software, Version 9.0.6; Stat ease Inc., 2015). These six-center point runs should be randomly conducted.

Table 3.3 Process variables and their limit values.

Name	Units	Type	Low	High
Reagent concentration (**A**)	Molar	Factor	0.01	0.60
O/A ratio* (**B**)	ml/ml	Factor	0.5	3.0
Contact time (**C**)	Min	Factor	10	120

Note: O/A ratio refers to the ratio of the volume of organic extractant (toluene) to volume of the acid solution used.

Table 3.4 Designed experiments using face-centered central composite design.

Run	Factor A: Extractant conc. (M)	Factor B: O/A ratio (ml/ml)	Factor C: Contact time (Min)
1	0.010	1.75	65
2	0.305	1.75	10
3	0.600	1.75	65
4*	0.305	1.75	65
5	0.600	3.00	120
6	0.010	0.50	10
7	0.010	3.00	10
8	0.305	1.75	120
9	0.010	0.50	120
10	0.305	0.50	65
11	0.600	3.00	10
12	0.600	0.50	10
13*	0.305	1.75	65
14	0.600	0.50	120
15*	0.305	1.75	65
16*	0.305	1.75	65
17	0.010	3.00	120
18	0.305	3.00	65
19*	0.305	1.75	65
20*	0.305	1.75	65

***** These designed points are center point replicates recommended by the software to ensure the repeatability, predictions, and accurate lack-of-fit test results

All twenty experiments were performed in random sequences to avoid or minimize the effects of uncontrolled factors. The results of the ICP-OES analysis are discussed in Chapter 4 and the effects of the three significant parameters on the extraction efficiency of each extractant are presented as well. The design points including the replicates are illustrated on the resulting graphs, showing the effects of different parameters on the extraction efficiencies. The verification points displayed on these graphs show how closely they agree with what are predicted by the mathematical models. The replicate points can specifically help the software to measure the accuracy of the predicted models and their pure errors. When the results of the replicates are not quite similar, they affect the accuracy of the models, which can be observed in the ANOVA tables presented in Appendix A.

3.6 Prediction of hazardous metals removal using Design Expert®

Design Expert® software was employed to develop polynomial models to predict the behaviour of the selected metals removal using the three extractants Aliquat336, Alamine308, and Alamine336. The fitted models are suitable resources to accurately predict the extraction process using parameter levels outside of the selected considered limits, and to determine the scale of importance of each parameter on the extraction efficiencies. A larger coefficient in these models represents a more significant effect of the respective parameter. The polynomial model's plus or minus signs for different coefficients represent negative or positive impacts of the respective parameters on the extraction efficiencies.

3.7 Analysis of variance (ANOVA)

A least-squares fit procedure was applied to estimate the coefficients of the polynomial for the targeted metals extraction using the three different extractants. Thereafter, based on the fitted surface responses, analyses were performed. The generated models developed by the Design Expert® software and their statistical importance were evaluated by the Fisher test (F-test) which is calculated by dividing the Model Mean Square by its Residual Mean Square for the analysis of variance (ANOVA). Analysis of variance evaluates the significance of the predicted models, as well as their accuracy. The detailed ANOVA results and tables are listed in Appendix A.

3.8 Optimization

Optimum conditions for metal extraction using either Aliquat336, Alamine308, or Alamine336, were determined using the optimization tool of the Design Expert® software. The objective of the programme is to optimize multiple responses, so that a "desirability function" between 0 and 1 can be maximized. The desirability function as defined by the Design Expert software is "*simply a mathematical method to find the optimum conditions. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The value is completely dependent on how closely the lower and upper limits are set relative to the actual optimum. The goal of optimization is to find a good set of conditions that will meet all the goals, not to get to a desirability value of 1.0*" (Design Expert® software, Version 9.0.6; Stat ease Inc., 2015). The minimum concentrations of the three extractants, O/A ratios, and contact times were targeted, to produce potentially the most

cost-effective hydrometallurgical process and to maximize the metal extraction efficiencies.

Chapter 4: Results and Discussion

4.1 Overview

The results obtained in this study are presented and explained in this chapter. Both leaching and solvent extraction results are discussed and the effects of different factors (contact time, extractant concentration, and the organic:aqueous ratio) on the process efficiency are illustrated as well. The results are rationalized and some analysis of variance (ANOVA) results are used to evaluate the significance of the results and of the developed polynomial models.

4.2 Spent catalyst characterization

Scanning electron microscopic (SEM) and energy dispersive X-ray spectroscopic (EDX) analyses were conducted on the surface of the spent HPC. Figures 4.1 and 4.2 show the results from both analyses. Coke, which is one of the main reasons for catalyst deactivation by covering its active sites, was identified as the elevated grey porous materials on the surface of the spent hydroprocessing catalyst and are circled for easy recognition. Furthermore, the SEM image shows that the powder is fairly homogeneous which ensures the accuracy of the leaching experiments.

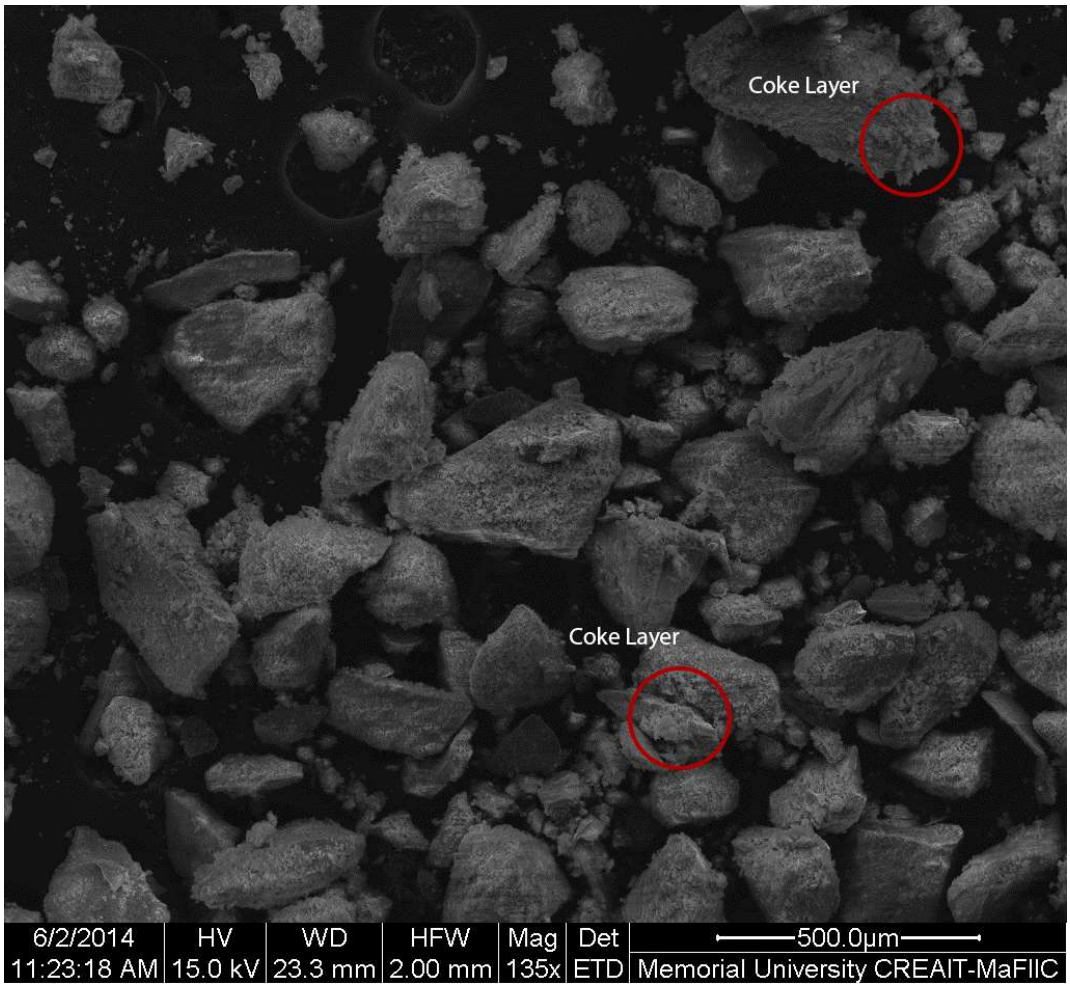

Figure 4.1 SEM image of powdered spent catalyst showing coke on active surface of the spent HPC sample used in this study.

The EDX analysis, conducted on the surface of the sample used in the present study, provided a typical composition of the spent HPC. The obtained metal list matched the MSDS provided by the North Atlantic Refining Limited.

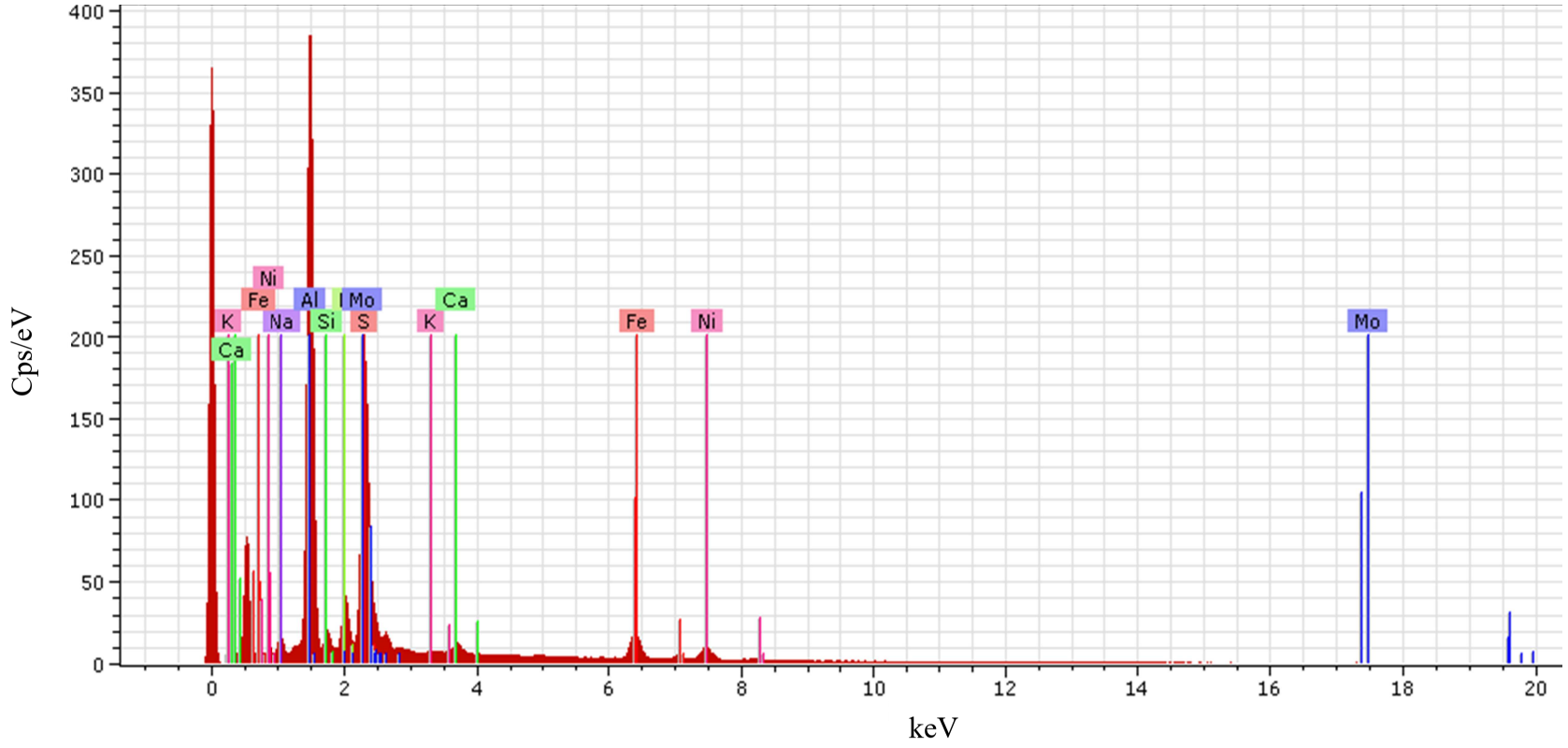

Figure 4.2 Energy Dispersive X-ray spectroscopy (EDX) on the spent HPC surface showing the metals identified.

4.3 Leaching results

The different acid leachate solutions obtained from the leaching of the spent catalyst powder using the three different acids used were analyzed by ICP-OES. The results for targeted metal quantities are listed in Table 4.1. Based on the results obtained in this study, aqua regia was considered to be the best leaching acid among the three acidic solutions used. Co, Ni and Mo all appeared to be better dissolved in the aqua regia than in the hydrochloric acid or nitric acid solutions. This could be due to the fact that strong oxidizers such as chlorine and nitrosyl chloride, are formed in aqua regia (Eq. 3) according to the following reaction (Mudroch et al., 1997):

$$HNO_{3\,(aq)} + 3HCl_{\,(aq)} \rightarrow NOCl_{\,(g)} + Cl_{2\,(g)} + 2H_2O_{\,(l)} \qquad \text{Eq. 3}$$

The strong oxidants can effectively dissolve the metals which are present as sulphides on the spent catalysts by oxidizing the sulfides to form sulfur, the metal ions thereby being easier to leach out into the aqueous acidic solution. The following reactions have been proposed for cobalt sulfide (Eq. 4) and nickel sulfide (Eq. 5) dissolution in aqua regia:

$$CoS + HNO_3 + 3HCl \rightarrow Co^{2+} + S + NOCl + 2Cl^- + 2H_2O \qquad \text{Eq. 4}$$

$$NiS + HNO_3 + 3HCl \rightarrow Ni^{2+} + S + NOCl + 2Cl^- + 2H_2O \qquad \text{Eq. 5}$$

Molybdenum sulfide can be dissolved in nitric acid and aqua regia (Abramov and Avdohin, 1998), presumably by a similar reaction, but is much less soluble in hydrochloric acid, as can be seen from Table 4.1.

The pH and electrical conductivity of the produced aqua regia after dissolution of the spent catalyst were measured to be 0.10 and 1.828×10^5 µS (micro Siemens) respectively, which show the high degree of acidity and ionic activity of the solution. The fresh aqua regia and the leachate solution (with aqua regia) after vacuum filtration are illustrated in Figure 4.3.

Table 4.1 Leached amounts (in mg/L) of spent HPCs metals in three different acidic solutions.

Metals leached / **Acid used**	**Cobalt (mg/L)**	**Molybdenum (mg/L)**	**Nickel (mg/L)**
Aqua regia	3643	840	1666
Nitric acid	<125	557	411
Hydrochloric acid	<125	<125	565

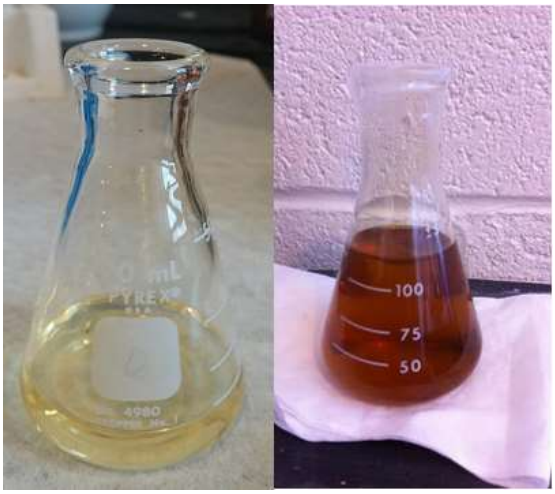

Figure 4.3 *Left*: Freshly-prepared aqua regia. *Right*: Leachate after dissolution of spent HPC sample.

4.4 Solvent extraction results

Table 4.2 lists the results for Co, Ni and Mo extraction percentages for all three of the extractants employed. The results obtained were based on the ICP-OES results from the aqueous solutions remaining after the solvent extraction process and comparing them to the initial aqua regia leachates of HPCs. In most cases, the leachates were diluted with deionized water prior to ICP-OES determination. The solvent extraction experiments were conducted based on the experimental design table (Table 3.4). It can be inferred from the table that Co is extracted the most efficiently of the three metals.

Aliquat336 is a quaternary tetraalkylammonium salt which is capable of extracting cationic species including Co and Mo from aqueous solutions into an organic solvent medium, and has been used in many different applications. Quaternary alkyl ammonium salts such as Aliquat336 are able to isolate metal complexes by a cation exchange mechanism, the long-chain C-8 alkyl groups making the salt lipophilic and consequently soluble in an organic solvent. In fact, tri- and tetraalkylammonium salts have had extensive use as phase-transfer reagents or catalysts for facilitating the transfer of ionic species from aqueous solutions into an organic solution.

On the other hand, Alamine308 and Alamine336 are both trialkylamines which contain basic tertiary nitrogen atoms, which can react with different types of acids such as HCl to form the corresponding quaternary trialkylammonium salts. The resulting ammonium salts are also able to undergo ion-exchange reactions with different types of cations (Sahu et al., 2013), as do quaternary alkylammonium salts such as Aliquat336.

Table 4.2 Experimental results obtained by ICP-EOS based upon the designed experiments shown in Table 3.4 for Co, Ni and Mo extraction.

Run	Aliquat336			Alamine308			Alamine336		
	Cobalt %	Nickel %	Molybdenum %	Cobalt %	Nickel %	Molybdenum %	Cobalt %	Nickel %	Molybdenum %
1	99.8	51.9	46.0	99.6	94.4	54.4	99.6	83.2	77.3
2	99.8	51.2	97.7	99.6	94.1	96.2	99.6	42.2	88.1
3	96.7	51.3	99.2	99.6	82.9	98.1	99.6	83.3	98.1
4	99.8	51.8	97.6	99.6	82.8	96.7	99.9	84.3	96.5
5	99.8	49.8	99.7	99.6	82.3	96.4	99.6	37.7	99.4
6	99.8	52.6	31.0	99.6	94.2	50.0	96.9	93.0	50.9
7	99.8	53.1	55.2	99.6	94.3	56.6	99.6	81.1	10.0
8	99.8	51.6	97.9	99.6	83.0	96.5	99.9	81.4	89.3
9	97.9	47.3	25.0	99.6	94.3	50.8	99.6	94.4	51.5
10	99.8	50.7	89.2	99.6	94.1	86.1	99.9	94.5	85.4
11	99.8	50.3	99.7	99.6	82.2	96.1	99.9	80.00	99.4
12	99.8	52.0	89.4	99.6	94.1	91.5	99.6	81.4	78.3
13	96.0	48.7	97.8	99.6	83.3	96.7	99.6	40.3	91.6
14	99.8	51.3	95.9	99.6	83.4	94.9	99.6	94.4	92.5
15	99.8	50.3	97.9	99.6	82.6	96.5	99.6	94.4	96.2
16	99.8	50.4	97.8	99.6	82.4	96.4	99.6	94.1	95.3
17	99.8	51.7	61.0	99.6	83.5	78.7	99.6	83.5	78.5
18	99.8	50.1	99.1	99.6	94.0	97.6	99.7	41.5	96.1
19	99.8	51.2	97.8	99.6	82.9	96.4	99.6	92.2	95.3
20	99.3	51.0	97.8	99.6	83.0	96.6	99.6	87.4	96.3

Based on the solvent extraction results, Aliquat336 was able to extract Co and Mo with up to 99 % efficiency but produced poor results for the removal of Ni, with the best efficiency being only 53 % (Runs # 6 and # 7). On the other hand, both of the tertiary amine-based extractants were generally able to remove all three of the targeted metals more effectively. With Alamine308 and Alamine336 respectively, however, Mo and Ni were not effectively extracted under some conditions. Extraction values under 60% were found for these metals, as shown in the table for Runs # 1, 6, 7, 9 and 17 (for Mo extraction by Alamine308); and Runs # 2, 5, 13 and 18 (for Ni extraction by Alamine336).

4.5 Effect of Aliquat336 on Co, Ni and Mo removal

According to the results, it is obvious that Co can essentially be quantitatively extracted even by using a diluted organic phase of Aliquat336. The various parameters which were examined had no effect on Co extraction which shows that the mass transfer resistance is quite low. The extraction of Co by Aliquat336 also occurs very rapidly and the maximum efficiency for Co extraction into the organic phase is reached within the first 10 min. The same patterns were observed for both Ni and Mo.

As discussed in Chapter 3, the design points are also illustrated on each of the following nine graphs of the effects of the different parameters on the metals extraction by Aliquat336, most of which are in agreement with the predicted models. The one or two replicate design points for Co can be considered outliers, as four or five of the replicates are consistent with the predicted model. A few design points for Ni extraction do not agree with its predicted model while design points for Mo perfectly match the predicted model for all three significant parameters affecting Mo extraction. This can also be observed in

the ANOVA tables (Appendix A) where R^2 values for Ni and Mo are completely different and are calculated as 0.61 and 0.99 respectively, showing great accuracy for the Mo predicted model. The dotted lines on the plots shown below represent the 95% confidence band on the mean prediction at any given contact time or reagent concentration or O/A ratio, which convey the certainty in fitting.

4.5.1 Effect of Aliquat336 concentrations

Figures 4.4, 4.5, and 4.6, show the results for experimental Runs # 1, 3, 4, 13, 15, 16, 19 and 20 for Ni and Co extraction. The efficiencies remain unchanged with increasing Aliquat336 concentrations in toluene but with the same O/A ratios and contact times. However, Mo extraction increases to reach a maximum value, and then slightly decreases. This decrease could possibly be due to the reversal of the equilibrium after 10 min or due to errors in experimental results; however, this decrease has little impact on the results and conclusions of this study. The improvement of Mo extraction with the larger extractant concentrations however, would be considered as being due to the increase of available Aliquat336 molecules to conduct the cation exchange mechanism with Mo complexes; On the other hand; however, the lower concentrations of Aliquat336 proved to be sufficient for extraction of Co and Ni. Therefore, it can be concluded that the larger Aliquat336 concentrations have little impact on the extraction efficiencies of Co and Ni, respectively. The optimum concentration of Aliquot336 is shown to be ~0.48 M.

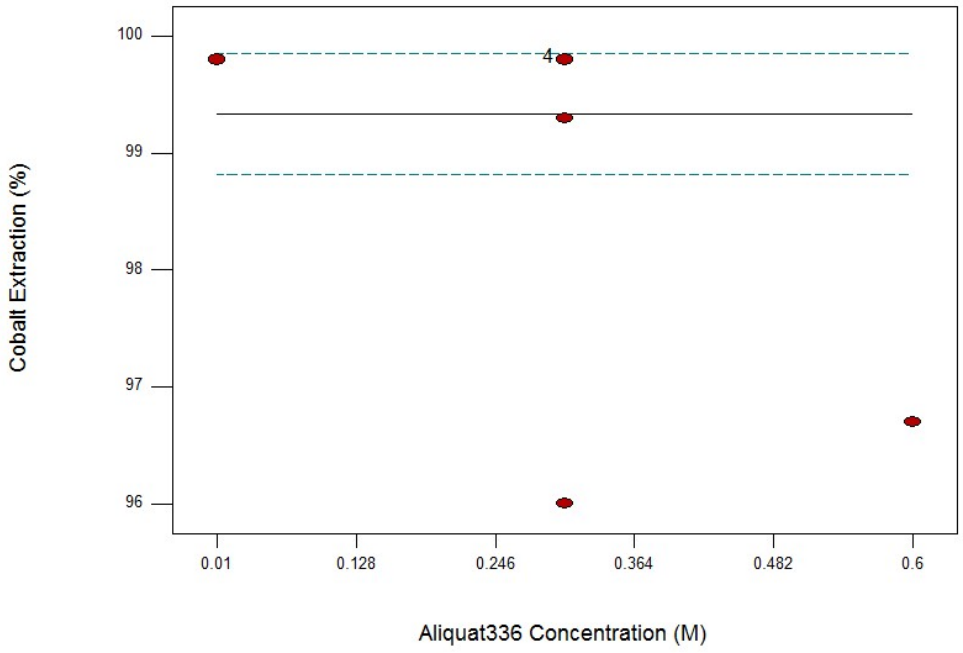

Figure 4.4 Changes of extraction efficiencies for Co with the changes in Aliquat336 concentrations (O/A ratio 1.75 and contact time 65 min).

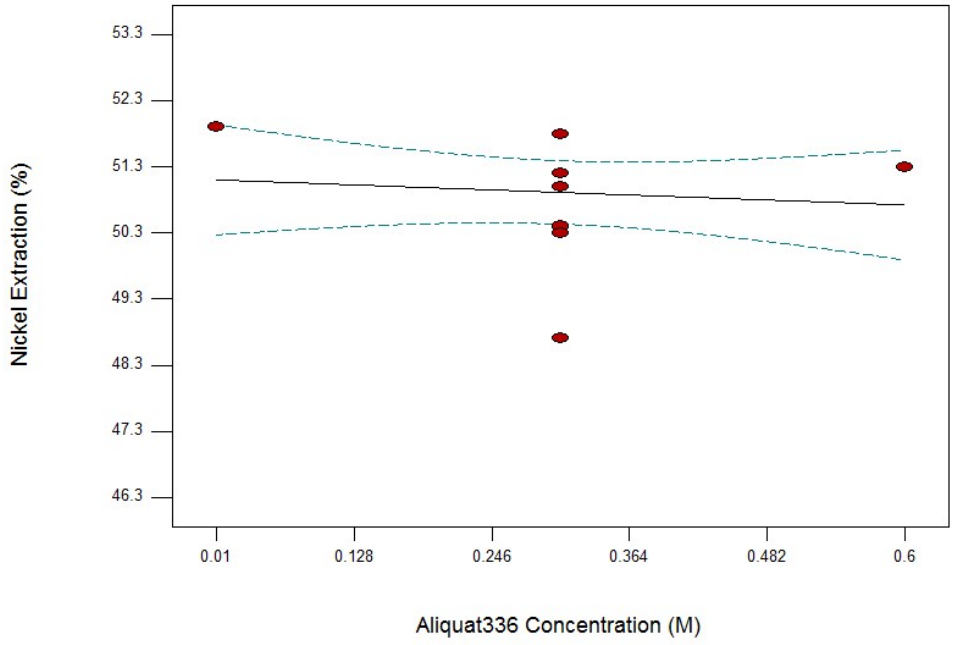

Figure 4.5 Changes of extraction efficiencies for Ni with the changes in Aliquat336 concentrations (O/A ratio 1.75 and contact time 65 min).

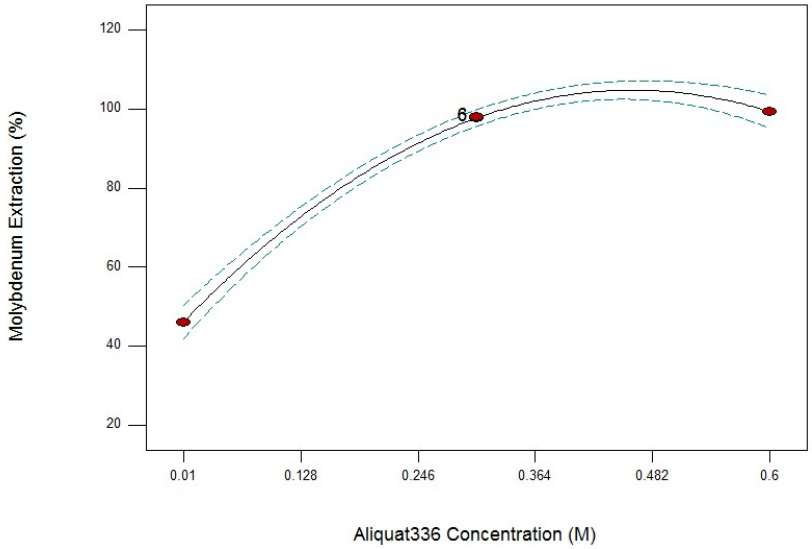

Figure 4.6 Changes of extraction efficiencies for Mo with the changes in Aliquat336 concentrations (O/A ratio 1.75 and contact time 65 min).

4.5.2 Effect of organic:aqueous (O/A) ratios

Figures 4.7, 4.8, and 4.9, illustrate the effects on the metals extraction efficiencies due to the ratio of the volumes of organic solvent, toluene ("O") to acid ("A") employed in this study, i.e. O/A ratio vs. different extraction efficiencies. The figures show the results for experiments runs # 4, 10, 13, 15, 16, 18, 19 and 20. Similar extraction values were observed for Co and Ni as there is little change with different O/A ratios; however, for Mo, the extraction efficiency increases by enriching the organic phase with Aliquat336, until a maximum amount is reached (Figure 4.6). Thus as the O/A ratio increases, the number of Aliquat336 molecules relative to the Mo ions in the aqueous solution increases as well and therefore, the extraction of the Mo from the aqueous solution into the organic phase increases. In the case of Co and Ni, on the other hand, a low concentration of Aliquat336 is sufficient for efficient removal of the Ni and Co from the aqueous solutions.

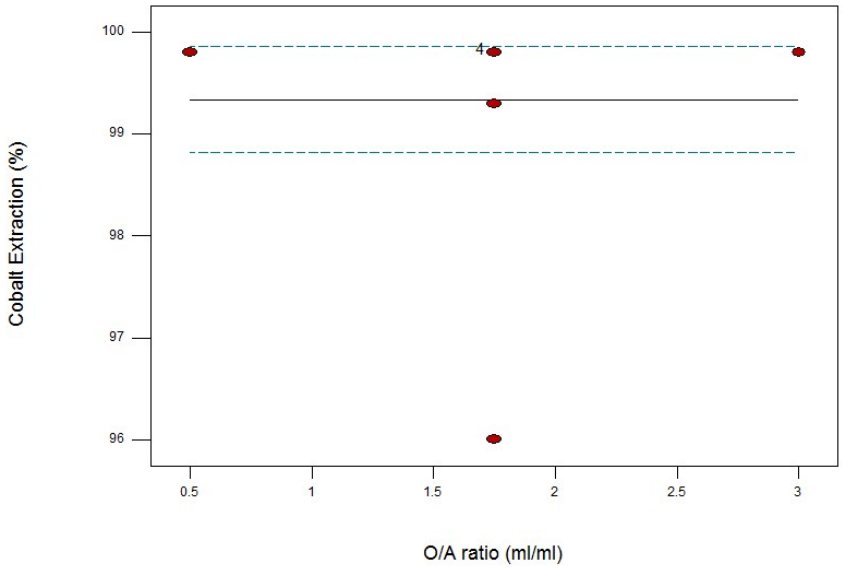

Figure 4.7 Effect of O/A ratios on Co extractions (Aliquat336 concentration 0.305 M and contact time 65 min).

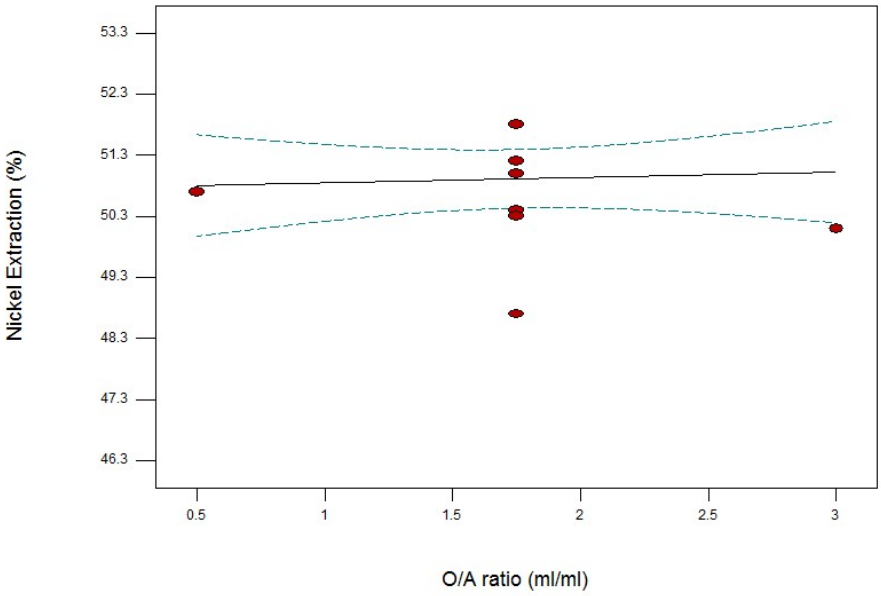

Figure 4.8 Effect of O/A ratios on Ni extractions (Aliquat336 concentration 0.305 M and contact time 65 min).

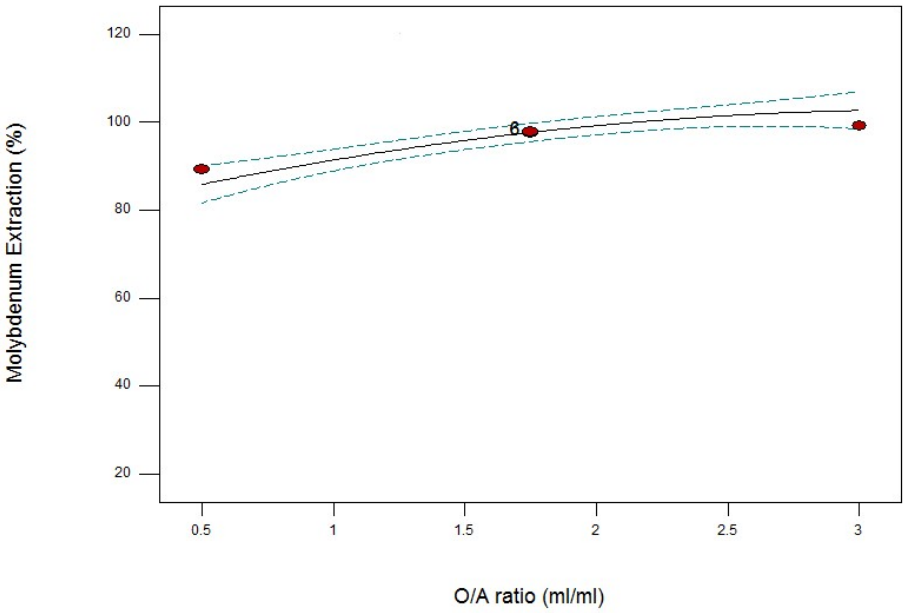

Figure 4.9 Effect of O/A ratios on Mo extractions (Aliquat336 concentration 0.305 M and contact time 65 min).

4.5.3 Effect of contact times

As illustrated in Figures 4.10, 4.11, and 4.12, (which show the results for the same experimental runs used in figures 4.7 – 4.9) the zero or negative slope after 10 min indicates that the contact time had no or adverse effect on efficiency. Only in the Ni extraction case, is a drastically decreased extraction observed with increased times of contact which suggests that optimum Ni extraction can be reached with only 10 min.

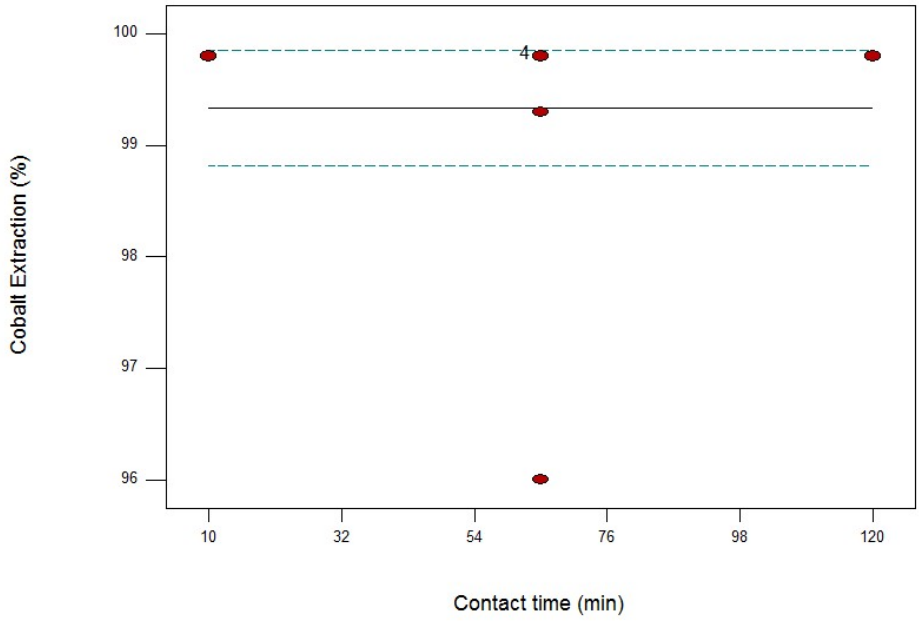

Figure 4.10 Co extractions vs. contact times (Aliquat336 concentration 0.305 M and O/A ratio 1.75).

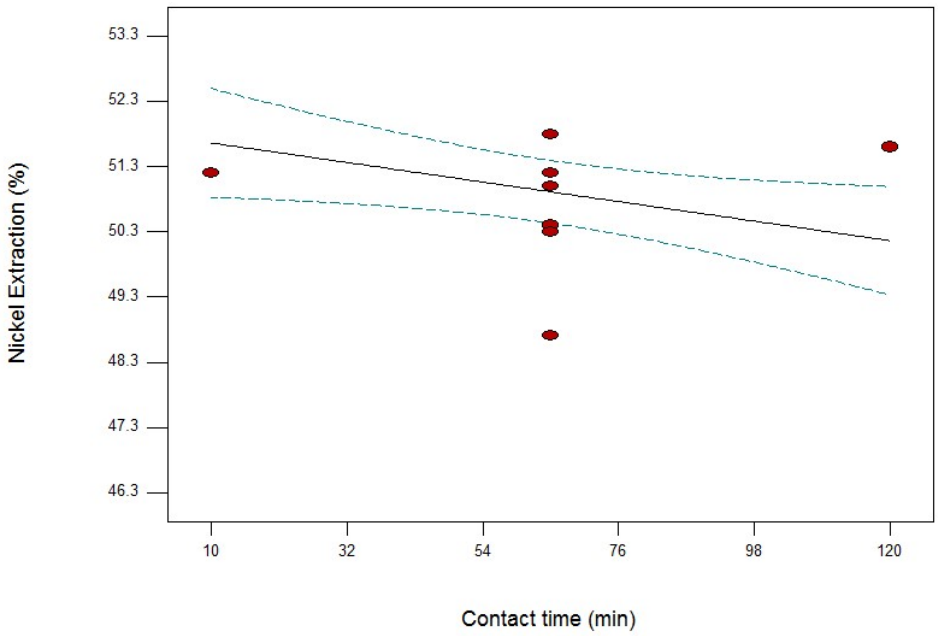

Figure 4.11 Ni extractions vs. contact times (Aliquat336 concentration 0.305 M and O/A ratio 1.75).

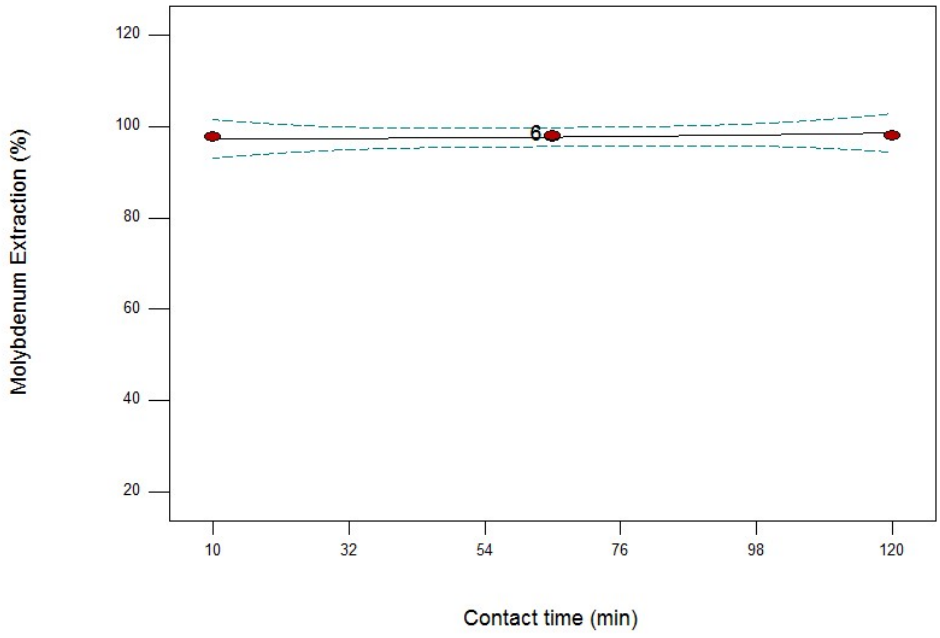

Figure 4.12 Mo extractions vs. contact times (Aliquat336 concentration 0.305 M and O/A ratio 1.75).

4.5.4 Prediction of Co, Ni and Mo removal using Aliquat336

Since Co extraction shows only slight changes with all of the modeled factors, there is no polynomial model developed for Co extraction efficiency and the system suggested only a consistent mean value for it. As for Ni, a two-factor interaction (2FI) and for Mo, a quadratic model was suggested from the results. The R^2 values were calculated to be 0.61 and 0.99 for Ni and Mo, respectively, which show that the most accurate model from the Design Expert® software is produced for the Mo extraction. All the models (in term of coded factors) are listed below for Ni and Mo extractions (Equations 6 and 7, respectively). The Mo extraction was found to be problematic since there are many factor interactions. Statistical modeling obtained by the Design Expert® software using a CCD approach shows

that the Ni and Mo solvent extractions are not solely dependent on the three main factors which have been identified, but also depend on other interactions. The coefficients represent the significance of various parameters, and according to the following equations, the most important interactions between these factors for Ni are those between the Aliquat336 concentration and the O/A ratio. The same pattern was obtained for Mo extraction. The results obtained helped to allow predictions to be made for the efficiencies when changes occur with some of the factors, and to predict the efficiency beyond the designed limits.

$$\text{Ni E\%} = [50.92+(-0.19\times A)+(0.11\times B)+(-0.75\times C)+(-1.01\times AB)+(0.69\times AC)+(0.51\times BC)] \quad \text{Eq. 6}$$

$$\text{Mo E\%} = [97.69+(26.57\times A)+(8.42\times B)+(0.65\times C)+(-5.76\times AB)+(0.84\times AC)+(0.66\times BC)+(-24.95\times A^2)+(-3.40\times B^2)+(0.25\times C^2)] \quad \text{Eq. 7}$$

4.5.5 Optimization

The optimum point for all these goals to be achieved was generated with a desirability of 0.823. For the optimum point, the Aliquat336 concentration is 0.24 M, the O/A ratio is 0.50 and the contact time is 10 min. The extraction efficiencies are predicted to be 99%, 52%, and 78% for Co, Ni and Mo extractions, respectively.

4.6 Effect of Alamine308 on Co, Ni and Mo removal

The extraction process for removing Co, Ni and Mo by Alamine308 was completed efficiently and rapidly. All three metals were extracted completely in the first 10 min using

low concentrations of the extractant. Unlike with Aliquat336, Co could also be extracted efficiently using Alamine308.

The design points on the following nine graphs of the different parameters' effects on the metals extraction by Alamine308 revealed graphs similar to those seen with Aliquat336 and as described in Chapter 3. The design points for Co and Mo match the predicted trends/models while the results of the design points for Ni do not match the predicted model, and show slight inconsistencies. This can also be observed in the ANOVA tables (Appendix A) where R^2 values for Ni and Mo are completely different and were calculated to be 0.47 and 0.98 respectively, showing low accuracy for Ni, but great accuracy for the Mo predicted models. The dotted lines represent the 95% confidence band on the mean prediction at any given contact time, reagent concentration, or O/A ratio, which convey the certainty in fitting.

4.6.1 Effect of Alamine308 concentrations

Figures 4.13, 4.14, and 4.15 illustrate the changes of extraction efficiencies (as shown from the same experimental runs which were shown previously in Figures 4.4 – 4.6) for the three targeted metals versus the concentration of Alamine308 in toluene at 65 min contact times. Maximum Co and Ni extraction can be achieved using a low concentration of Alamine308, but with more concentrated Alamine308 solutions, Ni extraction efficiency decreases drastically. Low concentrations of Alamine308 are not capable of removing all of Mo. With increasing the concentration, the efficiency increases to a certain point, and then starts to decrease. This could be due to the fact that with increasing the concentration of

Alamine308, the availability of its molecules for cation exchange increases and thus the extraction efficiency for Mo improves until a certain point where the maximum capability of Alamine308 to separate Mo cations is reached.

Since the trends for Ni and Mo extractions are completely different to that seen for Co extraction as a function of Alamine308 concentration, an optimum point may be determined to achieve acceptable extraction efficiencies for both of these metals. The overall pattern of metal extractions versus the Alamine308 concentrations is similar to that seen with Aliquat336; however, Ni extraction efficiency was significantly higher than the efficiency shown with Aliquat336.

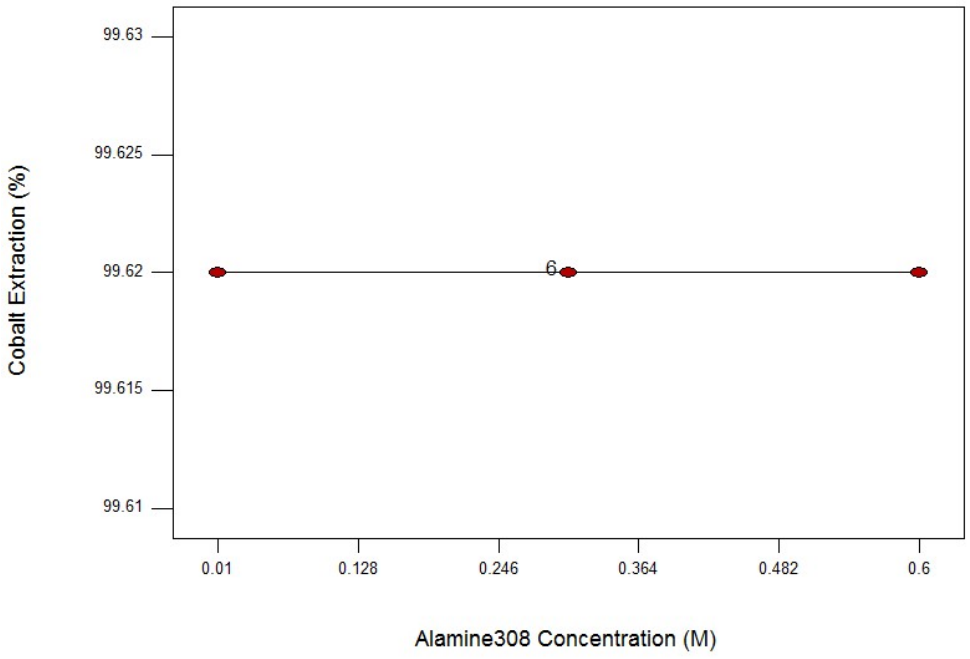

Figure 4.13 Change of extraction efficiency for Co with change in Alamine308 concentration (O/A ratio 1.75 ml/ml and contact time 65 min).

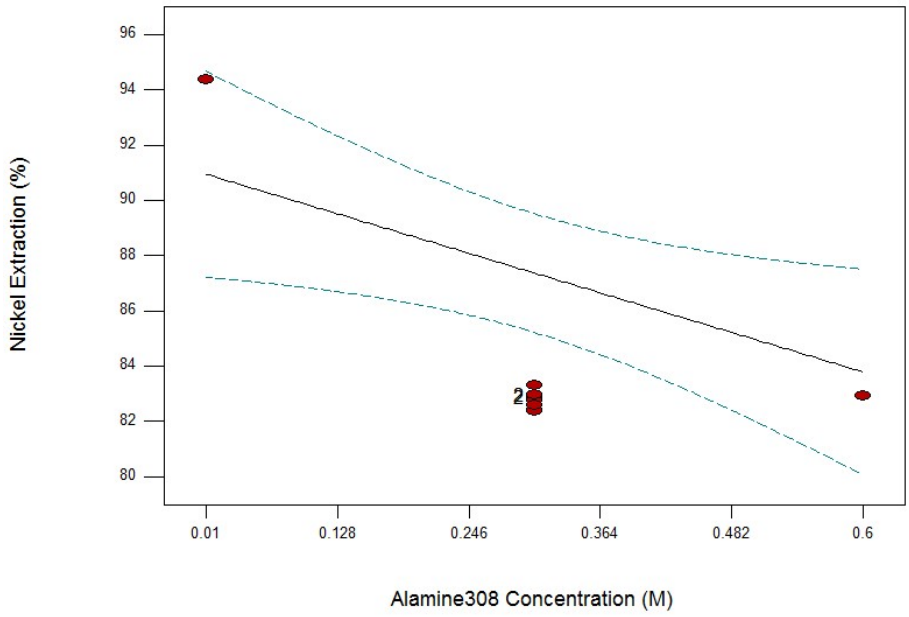

Figure 4.14 Change of extraction efficiency for Ni with change in Alamine308 concentration (O/A ratio 1.75 ml/ml and contact time 65 min).

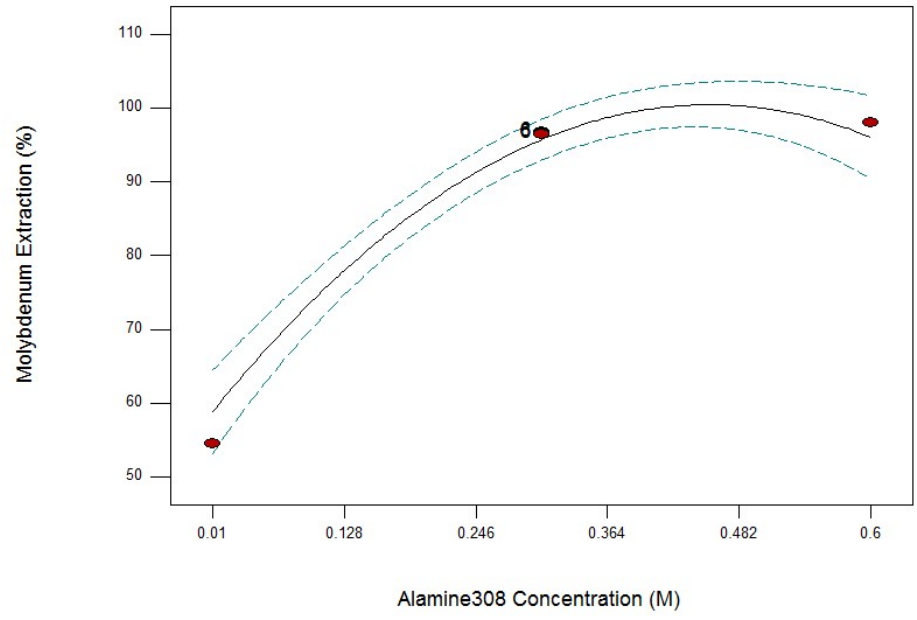

Figure 4.15 Change of extraction efficiency for Mo with change in Alamine308 concentration (O/A ratio 1.75 ml/ml and contact time 65 min).

4.6.2 Effect of organic:aqueous (O/A) ratios

The behaviour of Alamine308 for different metal extractions using different organic:aqueous (O/A) ratios is not completely similar to that seen for Aliquat336. Figures 4.16, 4.17, and 4.18 show the results from the corresponding data from 4.5.2 and Figures 4.7 – 4.9. These figures show that, although the Co extraction does not change and that the Mo extraction slightly increases with larger O/A ratios, Ni extraction efficiency decreases drastically, and that the maximum amount can be obtained with the lowest O/A ratio. Increasing the O/A ratio means there are more Alamine308 molecules accessible for cation exchange of Mo ions in the aqueous solutions, and similar to the effect of simply changing only the reagent concentration, Mo extraction efficiencies increase with increasing O/A ratios until a maximum is reached. Since dissimilar trends for Ni and Mo are observed with increasing O/A ratios, an optimum point may be determined for proper efficient extraction of both metals.

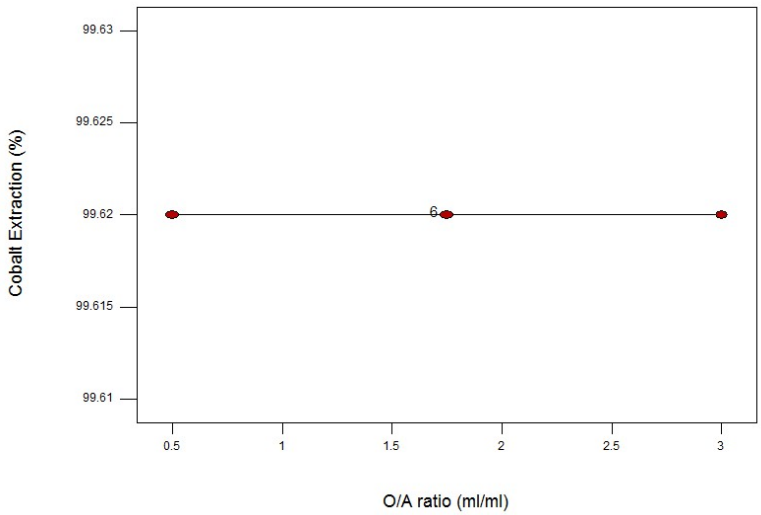

Figure 4.16 Effect of O/A ratio on Co extraction (Alamine308 concentration 0.305 M and contact time 65 min).

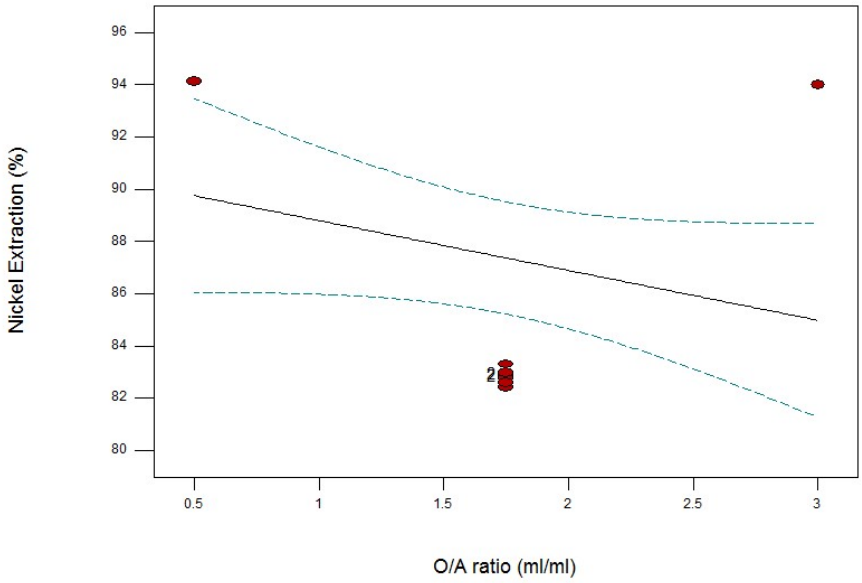

Figure 4.17 Effect of O/A ratios on Ni extractions (Alamine308 concentration 0.305 M and contact time 65 min).

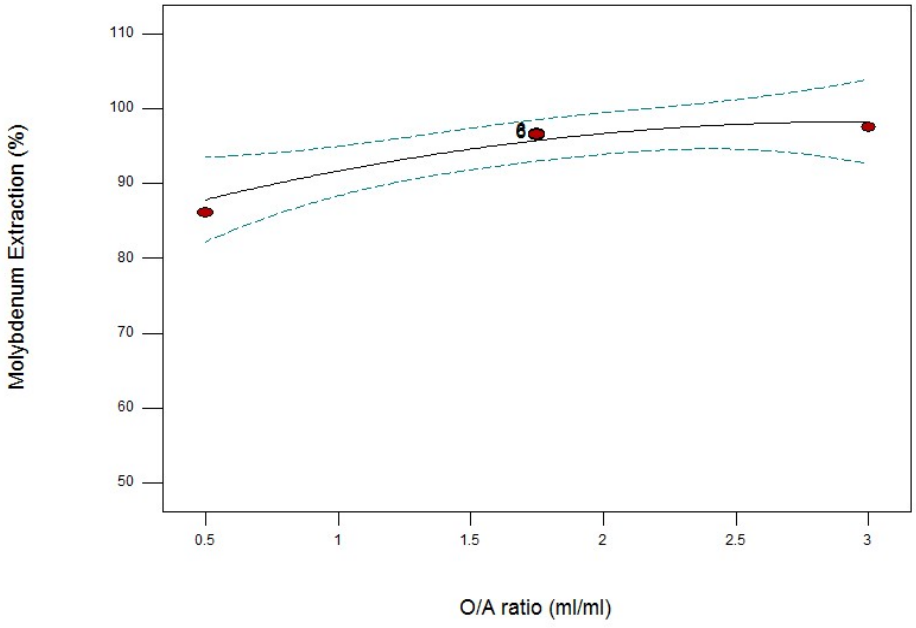

Figure 4.18 Effect of O/A ratios on Mo extractions (Alamine308 concentration 0.305 M and contact time 65 min).

4.6.3 Effect of contact times

The effect of contact times was measured for the different metals, and except for Mo, maximum efficiency can be reached after only 10 min. For Co, the extraction is the same and Ni extraction starts dropping drastically after 10 min, which suggests that for optimal Ni extraction, a 10-min contact time must be used. Mo extraction becomes slightly increased over time and the maximum extraction occurs at the end of the extraction time considered in this study (120 min). The general patterns for all metal extractions versus the contact time for Alamine308, as shown in Figures 4.19, 4.20, and 4.21, are similar to what was observed with Aliquat336; however, the amount of Ni extraction is significantly higher after 10 min (more than 90%).

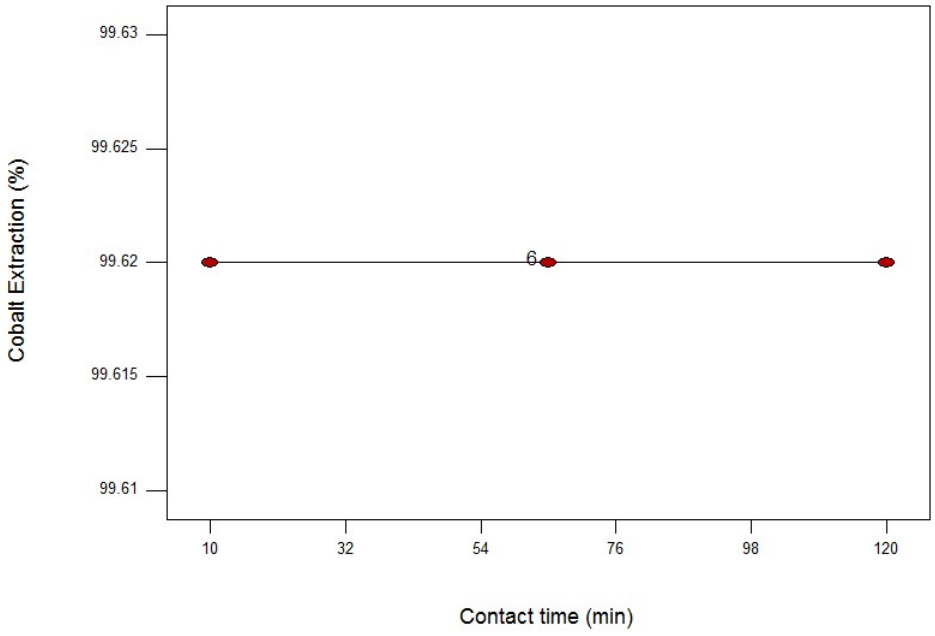

Figure 4.19 Co extractions vs. contact times (Alamine308 concentration 0.305 M and O/A ratio 1.75 ml/ml).

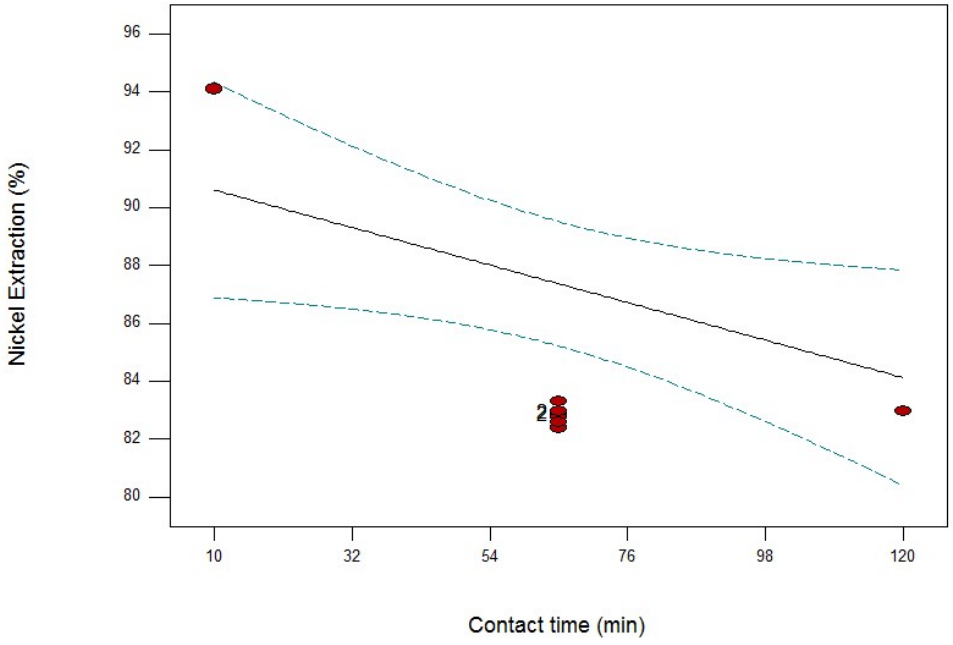

Figure 4.20 Ni extractions vs. contact times (Alamine308 concentration 0.305 M and O/A ratio 1.75 ml/ml).

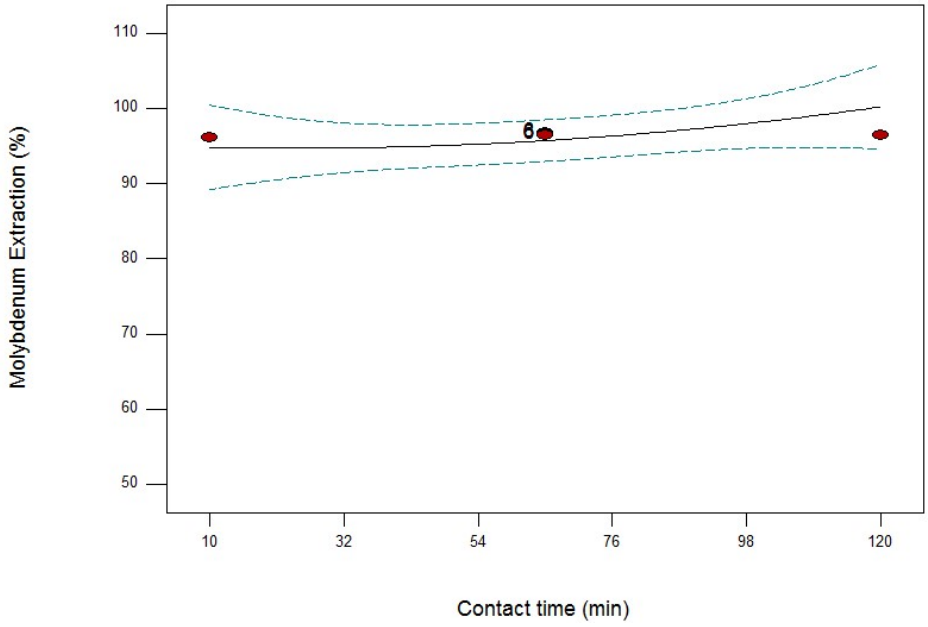

Figure 4.21 Mo extractions vs. contact times (Alamine308 concentration 0.305 M and O/A ratio 1.75 ml/ml).

4.6.4 Prediction of Co, Ni and Mo removal using Alamine308

For Alamine308, a mean model was suggested for Co extraction as it could be completely extracted in only 10 min using very dilute solutions. For Ni and Mo, linear and quadratic models were developed, and the R^2 values were calculated to be 0.47 and 0.98 respectively. It can be implied that the most reliable and accurate model is the one developed for Mo extraction. The fitted models for Ni and Mo removal by Alamine308 can be seen below as Eq. 8 and 9.

$$\text{Ni E\%} = [87.37 + (-3.58\times A) + (-2.39\times B) + (-3.24\times C)] \quad \text{Eq. 8}$$

$$\text{Mo E\%} = [95.75 + (18.63\times A) + (5.20\times B) + (2.70\times C) + (-3.55\times AB) + (-2.40\times AC) + (2.29\times BC) + (-18.30\times A\text{^}2) + (-2.70\times B\text{^}2) + (1.81\times C\text{^}2)] \quad \text{Eq. 9}$$

4.6.5 Optimization

The optimum point concentration calculated therefore, for Alamine308 is 0.23 M, the O/A ratio is 0.50 and the contact time is 10 min. The extraction efficiencies are predicted to be 99%, 94%, and 82% for Co, Ni and Mo extractions, respectively. A comparison between these results and the ones for Aliquat336 shows that Alamine308 is a better extractant as it can remove all the three targeted metals in 10 min with more dilute solutions than what is needed for Aliquat336. Aliquat336 is less effective in extracting Ni alongside Co and Mo.

4.7 Effect of Alamine336 on Co, Ni and Mo removal

Alamine336 was an efficient extractant in removing all three metals since only low concentrations were needed. The extraction time however, required for metal extraction using Alamine336 is greater than that required for the equivalent extraction using Aliquat336 and Alamine308. This should be considered a disadvantage for the use of Alamine336 to remove the hazardous metals from the spent HPCs used in this study.

Similarly, the design points are also illustrated on the following nine analogous graphs to those presented previously for Aliquat336 and Alamine308 for the different parameters' effects on the metals extraction by Alamine336. The design points for Co and Mo match the predicted trends/models while the results of the design points for Ni do not match the predicted model showing various inconsistencies. This can also be observed in the ANOVA tables (Appendix A) where R^2 values for Co, Ni and Mo are completely different and are calculated as 0.70, 0.28, and 0.86 respectively. Those values thus show very low accuracy for Ni, but roughly higher accuracies for the Co and Mo predicted models. The dotted lines on the graphs represent the 95% confidence band on the mean prediction at any given contact time, reagent concentration, or O/A ratio, which convey the certainty in the fitting.

4.7.1 Effect of Alamine336 concentrations

The effects of the Alamine336 concentration in toluene on the different metal extraction efficiencies are illustrated in Figures 4.22, 4.23, and 4.24 which are analogous to those shown in Figures 4.4 – 4.6 and 4.13 – 4.15. Co and Mo extraction follow a similar increasing trend with increasing the concentration of Alamine336 in the toluene solutions;

however, Ni extraction decreases using a more concentrated solution of Alamine336. Therefore, an optimum point of Alamine336 concentration may be determined for the most suitable extraction of all three metals. For Ni extraction, the effect of reagent concentration is similar to previous extractants which proves that a low extractant concentration is sufficient for Ni extraction and that greater concentrations of the extractant is unnecessary. The effect of concentration on Co and Mo is also similar to the observations described previously and shows that increasing the concentration of Alamine336 improves the availability of its molecules for the cation exchange process of Co and Mo ions until the maximum efficiencies are reached.

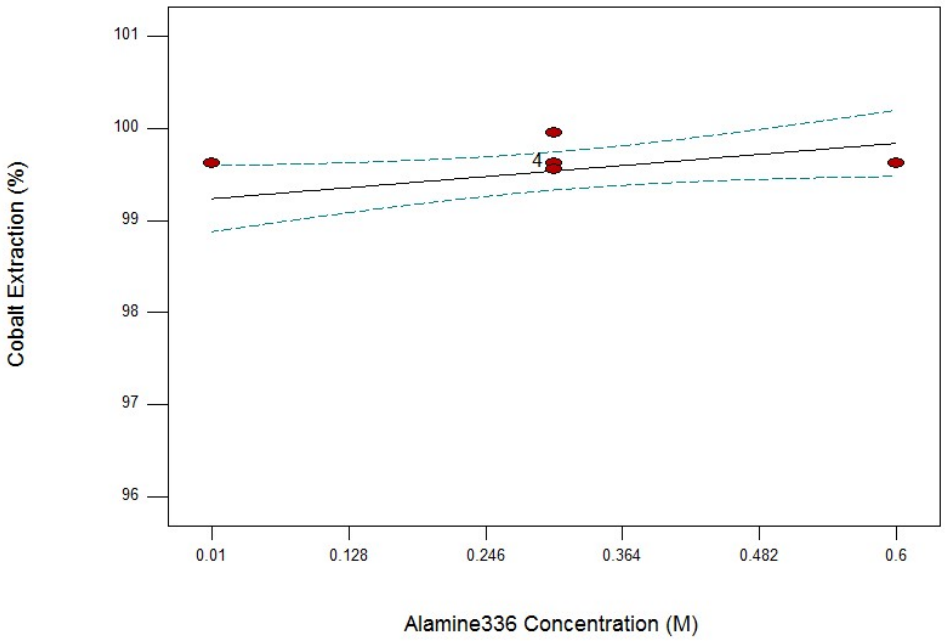

Figure 4.22 Change of extraction efficiency for Co with change in Alamine336 concentration (O/A ratio 1.75 ml/ml and contact time 65 min).

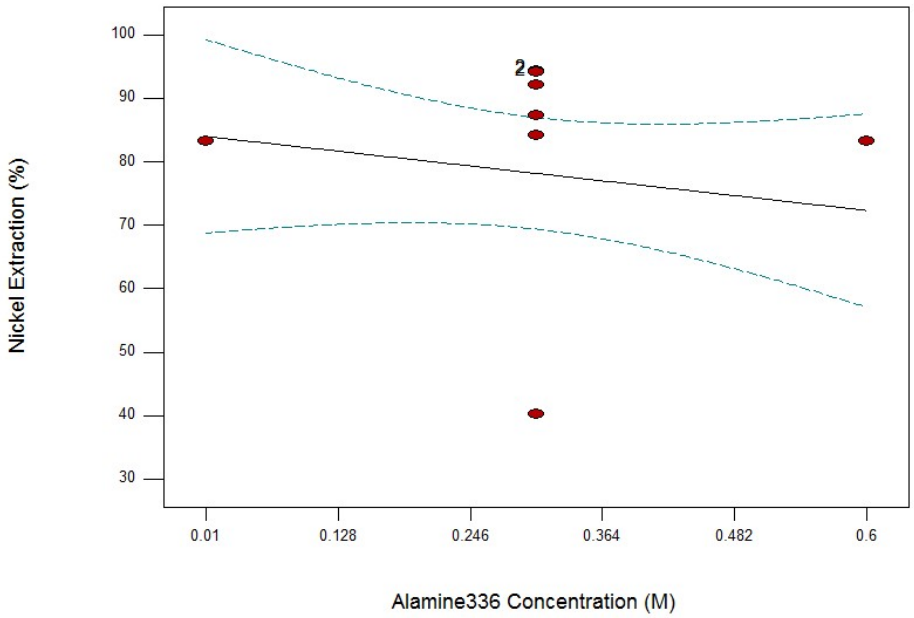

Figure 4.23 Change of extraction efficiency for Ni with change in Alamine336 concentration (O/A ratio 1.75 ml/ml and contact time 65 min).

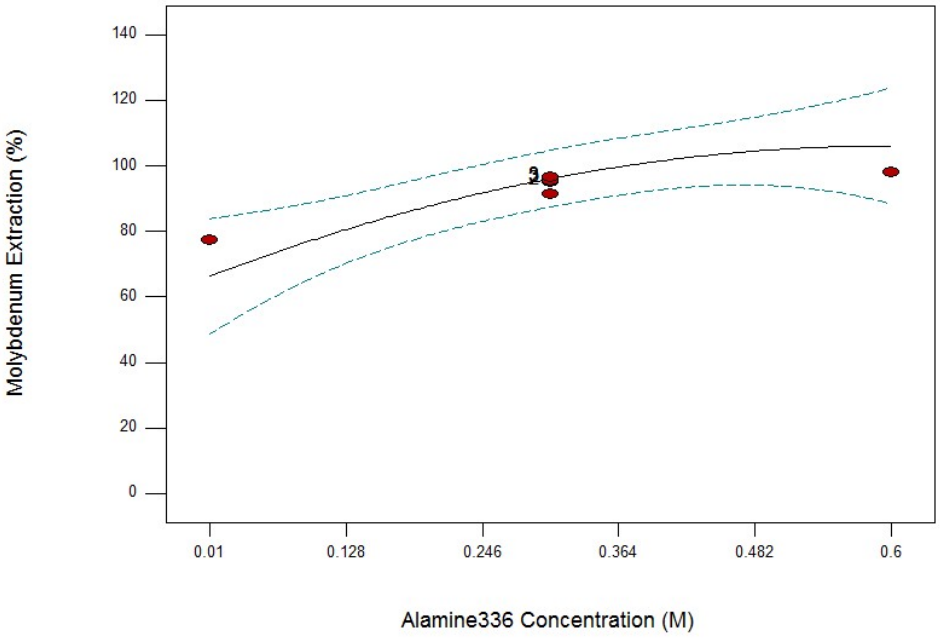

Figure 4.24 Change of extraction efficiency for Mo with change in Alamine336 concentration (O/A ratio 1.75 ml/ml and contact time 65 min).

4.7.2 Effect of organic:aqueous (O/A) ratios

Figures 4.25, 4.26, and 4.27 illustrate the effects of different O/A ratios on the three metal extraction efficiencies and correspond to Figures 4.7 – 4.9 and 4.16 – 4.18 respectively. Although both Co and Mo extractions increase with larger O/A ratios, the slope value of Co is higher, which suggests that the effect of the O/A ratio is more significant for Co extraction. Ni extraction decreases with increasing O/A ratios, which is similar to that found with both Alamine308 and Aliquat336.

The effect of O/A ratios on the metals removal is similar to the effect of Alamine336 concentration alone. This is due to the fact that by increasing O/A ratio, the availability of Alamine336 molecules in the organic phase for certain concentration of hazardous metals in the aqueous ratio increases as well, and that the extraction of the metals can be achieved using a greater number of accessible Alamine336 molecules in the organic phase.

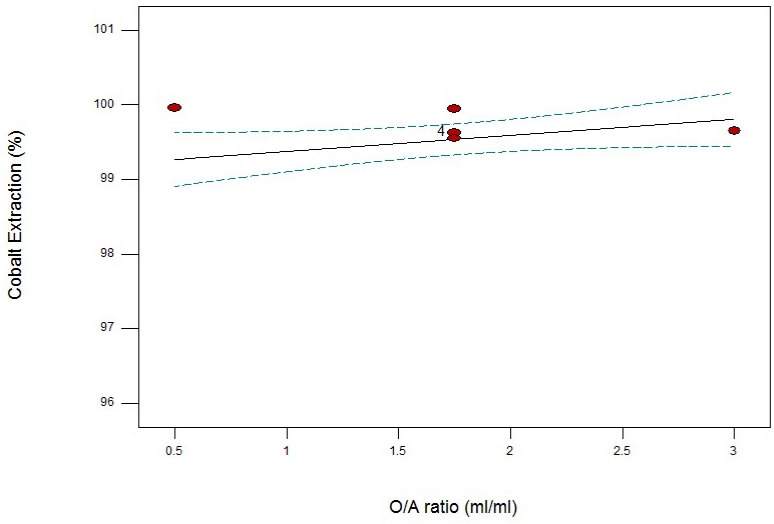

Figure 4.25 Effect of O/A ratios on Co extractions (Alamine336 concentration 0.305 M and contact time 65 min).

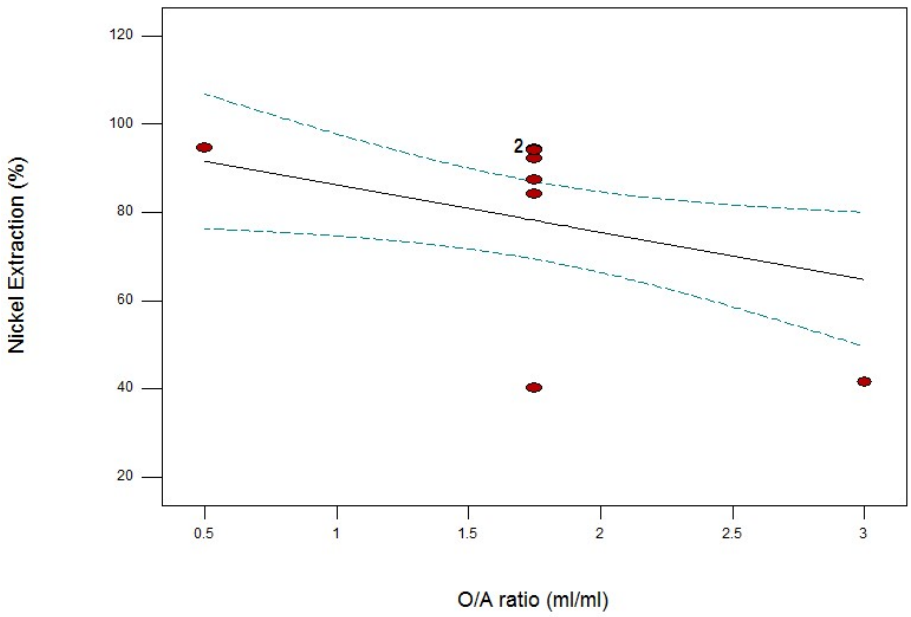

Figure 4.26 Effect of O/A ratios on Ni extractions (Alamine336 concentration 0.305 M and contact time 65 min).

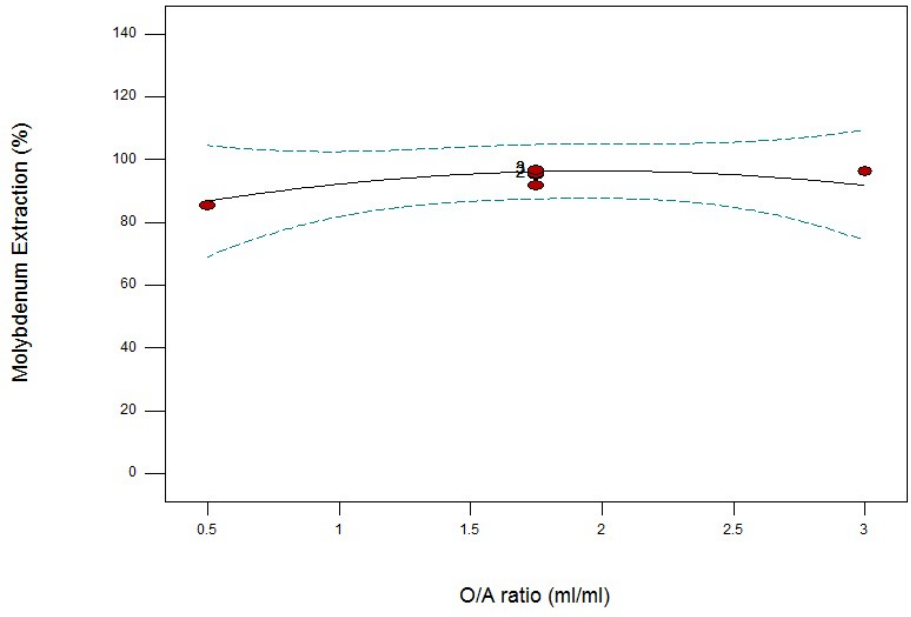

Figure 4.27 Effect of O/A ratios on Mo extractions (Alamine336 concentration 0.305 M and contact time 65 min).

4.7.3 Effect of contact times

The effects of contact times on the different metal extraction efficiencies using Alamine336 were determined and are illustrated in Figures 4.28, 4.29, and 4.30 and are once again analogous to those of Figures 4.10 – 4.12 and 4.19 – 4.21. All of the three targeted metal extraction efficiencies slightly increase with increasing contact time and, unlike with the other two extractants, 10 min is not sufficient to achieve maximum efficiency for their extractions. Therefore, the extraction time required for metal extraction using Alamine336 is greater than that required the equivalent extractions by Aliquat336 and Alamine308. This can be argued to be the major disadvantage of employing Alamine336 in the hydrometallurgical process used in this study for removing the hazardous metals from the spent HPCs.

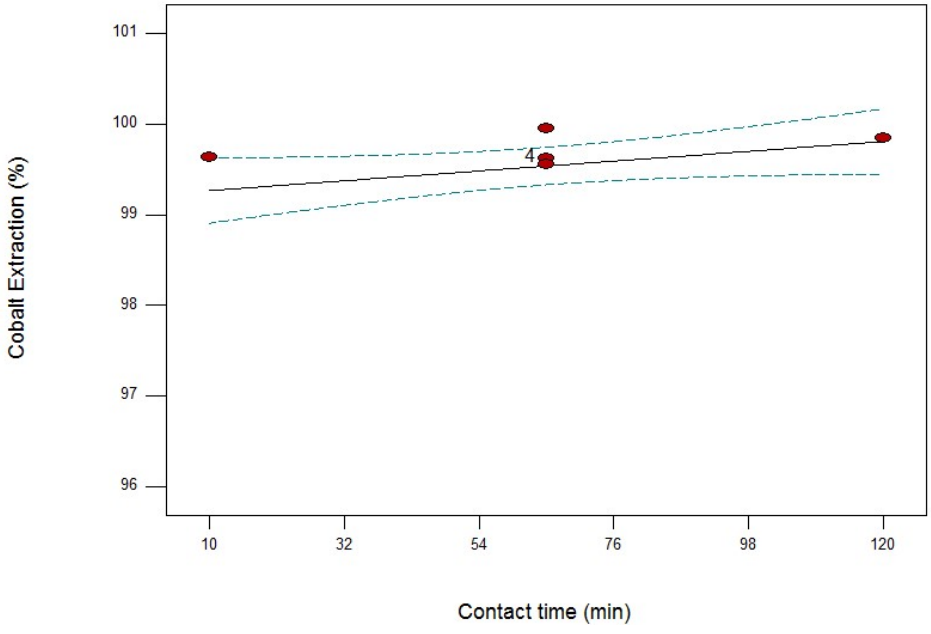

Figure 4.28 Co extractions vs. contact times (Alamine336 concentration 0.305 M and O/A ratio 1.75 ml/ml).

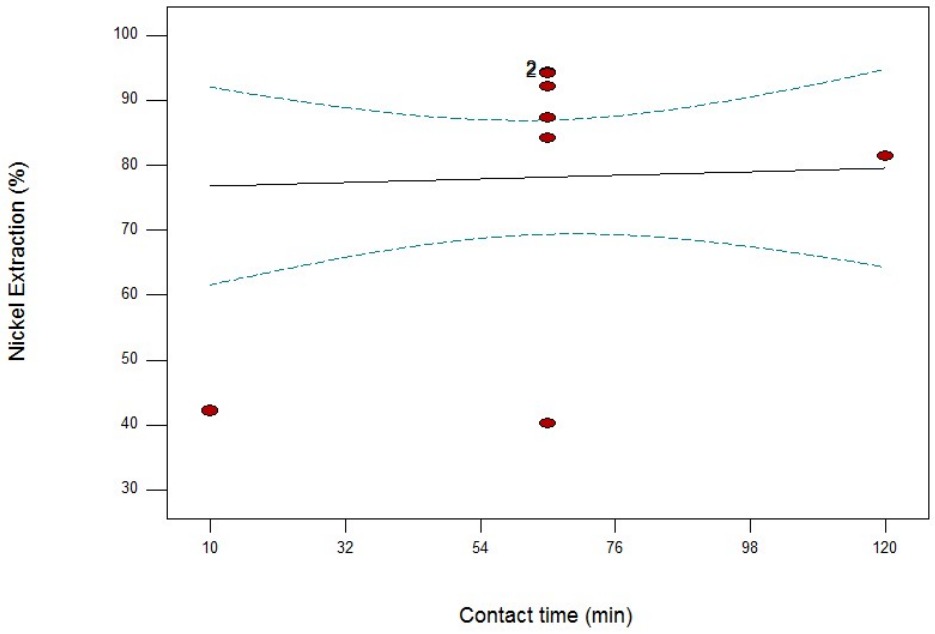

Figure 4.29 Ni extractions vs. contact times (Alamine336 concentration 0.305 M and O/A ratio 1.75 ml/ml).

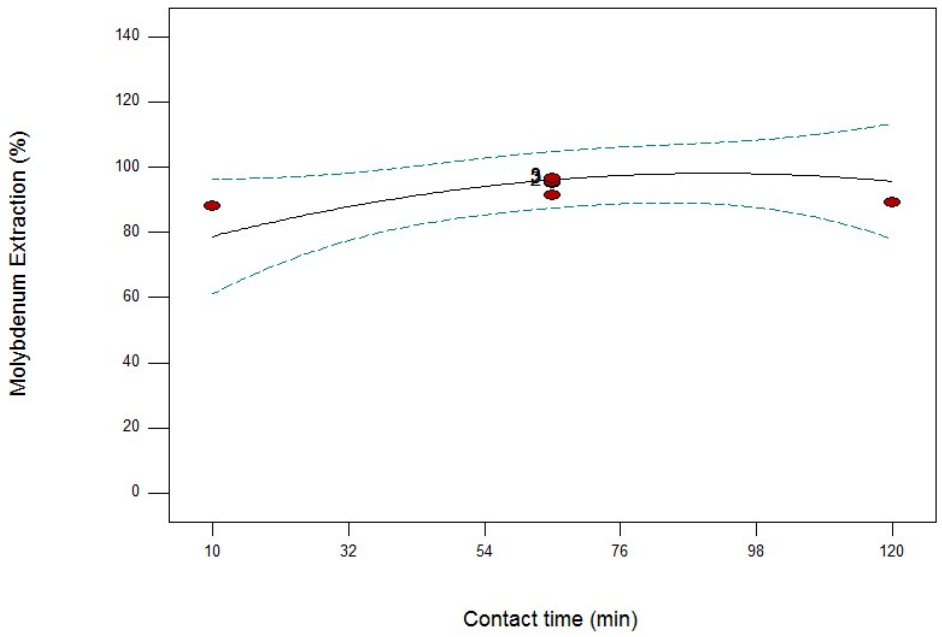

Figure 4.30 Mo extractions vs. contact times (Alamine336 concentration 0.305 M and O/A ratio 1.75 ml/ml).

4.7.4 Prediction of Co, Ni and Mo removal using Alamine336

For Alamine336, a two-factor interaction (2FI) model was developed with an R^2 value of 0.70 for Co extraction. Similar to Alamine308, linear and quadratic models were suggested for Ni and Mo with R^2 values of 0.28 and 0.86 respectively. The low reliability for Ni could be also observed in scattered design points in related graphs; All these fitted models for the respective metal removal by Alamine336 are shown in Eq. 10-12:

$$\text{Co E\%} = [99.54 + (0.30\times A) + (0.27\times B) + (0.27\times C) + (-0.32\times AB) + (-0.38\times AC) + (-0.38\times BC)] \quad \text{Eq. 10}$$

$$\text{Ni E\%} = [78.20 + (-5.84\times A) + (-13.40\times B) + (1.38\times C)] \quad \text{Eq. 11}$$

$$\text{Mo E\%} = [96.18 + (19.95\times A) + (2.49\times B) + (8.44\times C) + (5.25\times AB) + (-6.86\times AC) + (6.72\times BC) + (-9.95\times A\text{^}2) + (-6.88\times B\text{^}2) + (-8.92\times C\text{^}2)] \quad \text{Eq. 12}$$

4.7.5 Optimization

The same optimization procedures used for all of the other extractants was followed for Alamine336. For the optimum point, the Alamine336 concentration is 0.20 M, the O/A ratio is 0.50 and the contact time is 38 min. The extraction efficiencies are predicted to be 98.6%, 93.1 %, and 81.5% for Co, Ni and Mo, respectively. Although Alamine336 is a better extractant than Aliquat336 due to higher extraction efficiencies especially for Ni, its required contact time for removing all the targeted metals is 38 min, which makes it a less attractive extractant than Alamine308 which needs only 10 min.

4.8 Final remarks and other applications

Based on the results presented in this chapter, it can be concluded that Alamine308 could be considered to be the most efficient extractant to develop a hydrometallurgical method which is time- and cost-effective and also environmentally-friendly. The results of this study can be useful for developing a plant for treatment of spent HPCs as well as further research on metal separation and recovery from similar types of wastes. A few examples of such wastes can be other types of spent catalysts such as automobile catalytic converters containing valuable amounts of precious metals, solid waste produced in drinking water purification facilities, fly ash produced in thermal generating stations, electronic equipment wastes (e-waste), and other types of solid metal-containing wastes. Another potential application of the hydrometallurgical process developed in this study is that it can be employed to treat fluid or sludge wastes from acid mine drainage (AMD) and waste drilling muds (Acid mine drainage fact sheet, 2012); however, the application of such a hydrometallurgical approach for each of these different types of wastes should be investigated separately, and the processes should be optimized for the specific types of solid or liquid wastes. Therefore, more work needs to be done if the results of the current study are going to be used for other types of wastes. The complete conclusions of this study as well as the areas to further investigate are all discussed in Chapter 5.

Chapter 5: Conclusion

5.1 Concluding remarks

This study showed that all three investigated extractants have shown excellent abilities to extract the hazardous metals Co, Ni and Mo from spent HPCs, especially for Co and Mo. All extractants were capable of separating the metals from their aqueous (acidic) phase and transporting them into the extractant-rich organic phase. Alamine308 however, can be considered to be the most effective and suitable extractant for the spent HPCs examined in this study. Alamine308 is capable of effectively removing all three metals while for example, Aliquat336 is not as effective, especially for Ni extraction. Alamine308 is able to separate all of these metals from the aqua regia leachate within the first 10 min, whereas with Alamine336, more than 35 min was required. Modeling and optimization experiments were conducted using a central composite design (CCD) and the optimized conditions were calculated using Design Expert® software.

The following is a summary of key points addressed and the results obtained in this study:

- Hydrometallurgical methods to remove hazardous metals from spent catalysts have been studied as easy-to-implement, feasible, and environmentally-friendly processes such as solvent extraction (SX), ion exchange, and membrane separations.
- Among the extractants employed for our solvent extraction processes, Alamine308 is the most suitable extractant for metal removal from spent HPCs due to the short extraction time needed, low required organic:aqueous ratio, and high efficiencies toward all three targeted metals.

- Aliquat336 showed excellent potential to remove Co and Mo in 10 min but was unable to remove all Ni from the solid spent HPC which was examined in this study.
- Alamine336 was capable of removing all three targeted metals only after the 38 min which is the highest required extraction time among our three investigated extractants.
- Most of the polynomial models developed showed excellent predictability to determine the effects of different parameters and the extraction behaviour under different defined conditions.
- Models developed for Mo have been proven to be the most reliable and accurate models among the three targeted metals.
- This hydrometallurgical process would potentially be applicable for removal and recovery of precious and toxic metals from different types of solid waste; however, each process to treat specific wastes should be investigated independently.

5.2 Significant scientific findings

The hydrometallurgical process presented in this study was found to be able to remove the hazardous metals from the spent HPCs efficiently, using a cost-effective and environmentally-friendly process. The results of this study have improved understandings of the metal separation and recovery from secondary materials. The obtained results can be used as guides for further study on the scale-up and development of a pilot plant to remove hazardous metals from spent HPCs as well as other secondary materials using hydrometallurgical processes.

This study has developed a hydrometallurgical procedure with low required concentrations of Alamine308 and low required contact times for the optimized extraction of hazardous metals from spent HPCs. These findings could lead to improving the cost-effectiveness of such hydrometallurgical processes and to identify a possible efficient, cost-effective, and environmentally-friendly method to treat hazardous HPCs on a large scale and therefore, also reduce the potential impact of petrochemical activities on the environment. As well, the risks associated with the spent catalysts produced in such plants and their release to the environment can be reduced significantly.

5.3 New perspectives and recommendations

All of the extractants which were examined showed excellent capability for removing the target hazardous metals Co, Ni and Mo from the spent HPCs with very dilute solutions, in short periods of time. Since these results are from laboratory-scale experiments, it is strongly recommended that the possibility of a plant scale-up be investigated to gain a more practical understanding of how hydrometallurgical methods can be applied to solid waste management.

Furthermore, all of these experiments were only conducted under batch conditions. To achieve a complete understanding of how these results can be implemented in the industrial world, it is also necessary to conduct similar experiments under continuous conditions for which specific liquid-liquid extraction columns would be designed and tested.

Solvent stability and recovery is another aspect of future work, as it was not covered in this study. If solvents can be recovered by an easy-to-implement and cost-effective process, it can minimize the cost of the whole process. Stripping of the metals extracted into the

organic phase also needs to be investigated, including how the stripping agent can be recovered and recycled to reduce the operating costs. The solvent used in this study, toluene, is a relatively less toxic organic solvent but its stability under the aqua regia conditions needs to be determined. However, the short contact times and ambient temperature conditions would presumably mitigate against any oxidation side-reactions of the toluene.

Another potential improvement to the process would be the use of novel biosorbents for the metals removal. Although the use of the amine-based extractants in the dilute solutions used in this study may not be harmful, the use of biosorption processes can improve the environmentally-friendliness of such processes. Besides, biosorbents can be derived from different cheap biomaterials e.g. biochar or chitin which can improve the cost-effectiveness of the whole process.

Although the present work was concerned with the treatment of solid waste spent HPCs, there is still a significant amount of developmental work required if such a hydrometallurgical process is going to be implemented for spent HPCs or other secondary materials on a large scale. This includes how the metals can be recovered and purified from the organic solutions by stripping, precipitation, and/or electrowinning. Significant factors for those processes should be determined and their effects evaluated.

Since the characterization of spent HPCs differs for various petrochemical streams due to differences in employed fresh catalysts, different operational conditions and various feedstocks, it is highly recommended that each of the resulting spent catalyst types be characterized separately in order to develop a complete understanding of their composition

and other properties. A database of the spent HPCs under different streams and different operational conditions would therefore be an important requirement.

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Appendix A

ANOVA results

ANOVA results for the Ni and Mo extraction efficiency models for Aliqaut336 and Alamine308 are presented in Tables A.1, A.2, A.3, and A.4 respectively. The ANOVA results for Co, Ni and Mo extraction efficiency models are also listed in Tables A.5, A.6, and A.7 for Alamine336.

For all these models, low probability values imply that these models are significant for the 95% confidence interval as a P-value less than 0.05 indicates significance. As the P-value decreases, it becomes less likely that the effect is due to noise, and more likely that there was a real cause. For Aliquat336, there is only a 3% and 0.01% chance, for Alamine308, there is only a 1.54% and a 0.01%, and for Alamine336, there is only a 0.74 and 0.26%, chance that a "Model F-value" having the same great magnitude could occur due to noise. For all the three extractants, based on R^2 values, the most accurate model was developed for Mo extraction. The degree of freedom (DF) for each source is also listed in the table. In case of Alamine336, the model developed for Ni extraction has a P-value of 0.14, which is higher than the previous values for Ni extraction by the other two extractants and shows that this model is not as significant. Nevertheless, this model was the best fit among possible models for Ni extraction for Alamine336.

Table A.1 Analysis of variance results for Ni extraction by Aliquat336 ($R^2 = 0.61$).

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob > F
Model	20.19	6	3.37	3.40	0.0304
Residual	12.85	13	0.99		
Lack of Fit	7.16	8	0.90	0.79	0.6377
Pure Error	5.69	5	1.14		
Correlation Total	33.05	19			

Table A.2 Analysis of variance results for Mo extraction by Aliquat336 ($R^2 = 0.99$).

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob > F
Model	11687.50	9	1298.61	178.03	< 0.0001
Residual	72.94	10	7.29		
Lack of Fit	72.89	5	14.58	1508.17	< 0.0001
Pure Error	0.048	5	9.667 E-003		
Correlation Total	11760.45	19			

Table A.3 Analysis of variance results for Ni extraction by Alamine308 ($R^2 = 0.47$).

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob > F
Model	290.31	3	96.77	4.70	0.0154
Residual	329.15	16	20.57		
Lack of Fit	328.66	11	29.88	304.83	< 0.0001
Pure Error	0.49	5	0.098		
Correlation Total	619.45	19			

Table A.4 Analysis of variance results for Mo extraction by Alamine308 ($R^2 = 0.98$).

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob > F
Model	5798.04	9	644.23	49.25	< 0.0001
Residual	130.80	10	13.08		
Lack of Fit	130.72	5	26.14	1580.96	< 0.0001
Pure Error	0.083	5	0.017		
Correlation Total	5928.84	19			

Table A.5 Analysis of variance results for Co extraction by Alamine336 ($R^2 = 0.70$).

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob > F
Model	5.50	6	0.92	4.98	0.0074
Residual	2.39	13	0.18		
Lack of Fit	2.29	8	0.29	13.95	0.0050
Pure Error	0.10	5	0.021		
Correlation Total	7.89	19			

Table A.6 Analysis of variance results for Ni extraction by Alamine336 ($R^2 = 0.28$).

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob > F
Model	2154.88	3	718.29	2.08	0.1431
Residual	5523.42	16	345.21		
Lack of Fit	3346.34	11	304.21	0.70	0.7125
Pure Error	2177.08	5	435.42		
Correlation Total	7678.31	19			

Table A.7 Analysis of variance results for Mo extraction by Alamine336 ($R^2 = 0.86$).

Source	Sum of Squares	DF	Mean Square	F-value	p-value Prob > F
Model	8151.96	9	905.77	7.06	0.0026
Residual	1282.12	10	128.21		
Lack of Fit	1264.93	5	252.99	73.59	0.0001
Pure Error	17.19	5	3.44		
Correlation Total	9434.08	19			

Appendix B

List of Publications and Presentations

The following publications are the results of our experimental research from which, some of the thesis chapters are taken in part.

1. Zadeh, S. S., Nejad, H. H., & Georghiou, P. E. (2015, July). Hazardous Metal Removal from Spent Hydroprocessing Catalysts. Poster presented at the International Conference of Environmental Protection and Remediation (ICEPR 2015), Barcelona, Spain.

2. Zadeh, S. S., Nejad, H. H., & Georghiou, P. E. (2014, October). Observations on Toxic Metal Removal from Spent HPCs for Aliquat 336. In Proceedings of Conference of Metallurgists (COM 2014), Vancouver, BC, Canada, ISBN: 978-1-926872-24-7.

3. Zadeh, S. S., Nejad, H. H., & Georghiou, P. E. Hydrometallurgical Removal of Cobalt, Molybdenum, and Nickel from Spent Hydroprocessing Catalysts, to be submitted to Environmental Engineering and Management Journal.